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(ORIGINAL COMMUNICATIONS)

(EIGHTH) INTERNATIONAL

Pure and  
OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

Proceedings: Vol. 12-13

SECTION Ve: PAINTS, DRYING OILS AND  
VARNISHES



476131  
1.7.48  
458922  
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VOL. XII



QD  
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1912  
v. 12-13

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# ESSAI & CRITIQUE DE LA METHODE McILHINEY POUR L'ANALYSE DE VERNIS GRAS

G. BOCHAND AND P. GILLET

*Puteaux, France*

## TABLEAU VERNIS GRAS

### *Distillation par la Vapeur d'Eau.*

#### GROUP I

Partie volatile  
Solvants volatils

#### GROUP II

Partie non volatile  
Solvants fixes  
Résines  
Gommes dures  
Huiles  
Matières siccativantes (pour mémoire).

### *Saponification Alcoolique suivie d'un Traitement Acide.*

#### GROUP III (insoluble A)

Solvants fixes  
Résines  
Gommes dures  
Acides gras

#### Soluble A

Glycérine

### *Traitement par l'Ether de Petrole*

#### GROUP IV (Insoluble B)

Acides oxydés  
Gommes dures

#### GROUP V (Soluble B)

Solvants fixes  
Résines  
Acides gras inoxydés  
Acides gras incomplètement oxydés



| <i>Traitement par Alcool A 85°</i> |               | <i>Nouvelle Saponification</i> |   |
|------------------------------------|---------------|--------------------------------|---|
| Insoluble C                        | Soluble C     | Insoluble D                    | Soluble D   |
| Gommes dures                       | Acides oxydés | Solvants fixes                 | Acides gras in-<br>oxydés d° in-<br>compl. oxydés     |
|                                    |               |                                | Résines   |
|                                    |               |                                | <i>Determines par<br/>la Methode<br/>Twitchell</i>    |
|                                    |               |                                | Résines   |
|                                    |               |                                | Acides gras<br>inoxydés and<br>incomplèt ox-<br>ydés. |

Pour fournir sur la méthode des critiques raisonnées, nous en avons fait l'application à l'analyse d'un vernis de composition rigoureusement connue & rentrant dans la série des fabrications courantes.

Voici quels ont été les résultats sur une prise d'essai de 13 gr., 616 de vernis:

|                                     |        |
|-------------------------------------|--------|
| Solvants volatils.....              | 44,70% |
| Glycérine.....                      | 1,80   |
| Gommes dures.....                   | 10,13  |
| Acides oxydés.....                  | 7,06   |
| Ac. inoxydés ou incomp. oxydés..... | 10,81  |
| Solvants fixes.....                 | 4,50   |
| Résines.....                        | 11,56  |
| Total.....                          | 90,56  |

Nous avons seulement remplacé la méthode de TWITCHELL par le procédé de HÜBL & STADLER qui nous semble d'exécution plus aisée & plus sûre.

Voici la composition initiale du vernis soumis à l'analyse :

|   |        |
|---|--------|
| Gomme dure, variété de Pontaniak cuite avec 17% |        |
| de perte.....                                   | 12,50% |
| Résine.....                                     | 12,50  |
| Huile de lin crue.....                          | 12,50  |
| Huile de bois polymérisée.....                  | 12,50  |
| Essence de térébenthine.....                    | 45,00  |
| Huile minérale légère.....                      | 5,00   |
| Total.....                                      | 100,00 |

La perte d'environ 10% de l'analyse se retrouve d'une façon assez constante dans le dosage de certains éléments :

|                 |       |            |        |
|-----------------|-------|------------|--------|
| Gommes dures,   | 10,13 | au lieu de | 12,50% |
| Résine          | 11,56 | d°         | 12,50  |
| Solvants fixes, | 4,50  | d°         | 5,00   |

L'analyse est très suffisamment approximative en ce qui concerne les solvants volatils (44,70% au lieu de 45%); pour les huiles l'erreur est grande, car nous trouvons 19,50% au lieu de 25,00%. Cela provient principalement de la nature des corps examinés & des difficultés matérielles des séparations par l'entonnoir à robinet, (gouttes huileuses que l'on ne peut détacher, émulsions partielles, difficultés de distillation des solvants, suintements sur les parois des vases, etc., etc.), toutes causes de pertes lorsqu'on effectue les pesées. Aucune des méthodes d'analyse proposées, soit pour le dosage de tous les éléments, soit pour la séparation de deux ou plusieurs d'entre eux, ne signale ces causes d'erreur dues aux difficultés de manipulation.

Un autre point faible du procédé McIlhiney réside dans ce fait que les gommes dures cuites ne sont point complètement insolubles dans l'éther de pétrole. Lorsque la gomme dure est faiblement pyrogénée, comme c'est le cas du vernis examiné, le pouvoir dissolvant de l'éther de pétrole est nul ou à peu près. Au contraire lorsque la pyrogénéation du copal est poussée assez loin, comme cela est souvent nécessaire, pour les gommes manilles, par exemple, la proportion de pyrocopal soluble dans l'éther de



pétrole croit dans de notables proportions; il s'ensuit que l'on pèse plus tard de la gomme dure comme résine.

## ETUDE DU GROUPE I

### *Solvants Volatils Entraînés par la Vapeur d'Eau*

On recherche généralement ces solvants ramenés aux 3 formes: carbures aromatiques, carbures terpéniques, carbures pétroliques.

Les solvants séchés aussi exactement que possible, sont traités par HCl gazeux sec qui fournit le mélange de chlorhydrates de térébenthènes solides & liquides que l'on peut aisément séparer des carbures benzéniques & pétroliques.

Les carbures benzéniques par un traitement acide nitrique & réduction ultérieure, permettent, par reprise acide, de donner des sels d'amine solubles dans l'eau, tandis que les carbures pétroliques résistant à cette action, se retrouvent à l'état insoluble.

Fréquemment les carbures pétroliques employés sous la dénomination de "White Spirit" proviennent des pétroles de Galicie & renferment une certaine quantité de carbures benzéniques ou cycliques. Dans ce cas, il y aura attaque nitrique partielle & incertitude dans le dosage.

Disons toutefois que la nature du solvant volatil entrant dans la composition du vernis est la chose qui intéresse le moins le fabricant, en ce sens qu'elle n'influe que très peu sur la valeur finale du produit: brillant, durée, souplesse ou dureté.

## ETUDE DU GROUPE II

### *Résidus de la Distillation à la Vapeur d'Eau.—Saponification Alcoolique Suivant d'un Traitement Acide*

La saponification s'effectue normalement. Le traitement acide par HCl de préférence, permet une séparation facile de l'Insoluble A (Acides gras, résines, gommes dures) d'avec le soluble A (eaux glycéreuses).

Dans le soluble A on dose la glycérine. Ce dosage est considéré actuellement comme sans intérêt par l'industrie.

## ETUDE DU GROUPE III

*Insoluble A du Groupe II.—Traitement par l'Ether de Petrole*

Ce traitement se fait facilement dans un appareil à épuisement, mais l'évaporation de la solution éthérée pour obtenir le soluble B est une opération fort délicate.

La grande cause d'insuccès est le suintement des parties solubles entraînées sur les parois intérieures & extérieures par l'évaporation de l'éther. Etude à faire: Méthode d'évaporation ou recherche d'appareil évaporatoire approprié supprimant les pertes par suintement.

## ETUDE DU GROUPE IV

*Insoluble B du Groupe III.—Traitement par l'Alcool à 85°  
(On obtient l'insoluble C & le soluble C)*

Ce traitement ne laisse pas complètement insolubles les gommes dures & dissoud incomplètement les acides oxydés. La variation dans le pourcentage peut aller de 5 à 6 en plus ou en moins, ce qui empêche de dire nettement si le vernis est à base d'huiles pures ou contient de la gomme.

La connaissance exacte du rapport des quantités d'huiles & de gommes contenues dans un vernis est de la plus haute importance pour le fabricant. C'est là le point faible de la méthode. De nouvelles études pour le dosage de ces deux éléments sont de toute nécessité.

## ETUDE DU GROUPE V

*Soluble B du Groupe III*

Une nouvelle saponification alcoolique du soluble B séparera les solvants fixes (Insoluble D) des résines acides gras inoxydés & acides gras incomplètement oxydés (soluble D).

Cette séparation se fait assez facilement, mais ce 2ème traitement alcoolique donne des savons inconnus, près de leur point limite de solubilité & empêchant une séparation nette dans l'entonnoir à robinet.

*Insoluble D.* Les solvants fixes extraits par cette saponification comportent les huiles minérales. Etant donné le groupe très



restreint de ces huiles employé dans l'industrie, il ne paraît pas utile de spécifier à quel genre d'huile minérale on a affaire.

*Soluble D.* Méthode TWITCHELL. A cette méthode d'une exécution fort délicate, nous préférons le procédé HÜBL & STADLER basé sur la solubilité du résinate d'argent dans l'éther, tandis que l'oléate d'argent y est insoluble. Cette méthode donne des résultats assez précis.

#### MATIÈRES SICCATIVANTES

Nous passons à dessein sous silence la recherche des composés minéraux introduits dans les vernis pour la siccativation des huiles. La quantité restant dans le vernis est pour la plupart des cas très inférieure aux proportions mises en oeuvre à la fabrication. Leur recherche & leur dosage sont du domaine de la chimie minérale.

#### CONCLUSIONS

Nous estimons que le procédé de Mr. McIlhiney ne permet pas de déterminer d'une façon suffisamment précise les constituants d'un vernis.

Les études à faire doivent porter sur les points suivants & dans l'ordre où nous les indiquons :

Connaissance exacte de la nature de la gomme dure employée, ce qui implique l'étude des propriétés des différentes gommes aux différents de rés de pyrogénéation.

Séparation exacte de la résine ordinaire d'avec le pyrocopal, quel que soit le degré de pyrogénéation de ce dernier.

Nature exacte de l'huile végétale employée et *accessoirement* :

Nature des huiles minérales.

Analyse complète des solvants volatils.

Ces études ne devront se terminer, en aucun cas par l'adoption de formules types de vernis, formules très appréciées des administrations. Si de telles formules étaient adoptées, il y aurait souvent présomption de fraude sur un vernis possédant toutes les qualités requises pour l'emploi que l'on en veut faire, si ses constituants ne correspondaient pas à la formule d'adjudication.

Les différentes proportions des constituants répondent à des nécessités industrielles & actuellement sont souvent les seules caractéristiques de la fabrication d'une marque connue.

## LAMP BLACK AND CARBON BLACK

GODFREY L. CABOT

*Boston, Mass.*

Lamp Black is defined in Webster's Dictionary as the fine, impalpable soot obtained from the smoke of carbonaceous substances which have been only partly burnt, as in the flame of a smoking lamp. This definition is correct from the chemist's point of view and covers also the substance that is known to the trade in this country and elsewhere as "Carbon Black." Nevertheless, I have given both names in the title to this paper, because in the American trade the term "Lamp Black" is usually understood to be a soot deposited by the smudge process and made from oil, resin or some other solid or liquid raw material; whereas Carbon Black is the term applied to a black deposited by actual contact of a flame upon a metallic surface.

Using the name "Lamp Black" in its wider sense as any commercial form of soot, it may be prepared in three different ways,—1st, by the combustion of dead oil of tar, pitch, resin or some other carbonaceous raw material with an inadequate supply of air and the collection of the floating particles of soot that escape unburned from the flame and slowly deposit themselves on the walls and floors of the collecting chambers.

2nd,—it may be formed by the direct impact of a flame upon a collecting surface and 3rd, it may be formed by heating carbonaceous vapors to a decomposing point, apart from the air or flame.

From time immemorial soot has been used by some savage tribes to paint their faces with and color other objects that they might wish to beautify in this way, but the civilized man has long since discarded ordinary soot as being too impure, gritty and weak in coloring power and to the best of my knowledge, there is no market for ordinary soot for paints, printing ink or any of the uses to which Lamp Black is commonly applied.

Ordinary soot contains 50% of grit, empyreumatic matter and other impurities.

Considering Lamp Black in the more restricted sense to which it is known to the American trade, of a commercial soot, deposited by the smudge process, the starting point is usually the dead oil of tar, an oil containing a large amount of naphthalene, a certain amount of phenol and various aromatic hydrocarbons particularly suited to the manufacture of Lamp Black by reason of the large percentage of carbon therein contained, the effect of which is that when burnt with an inadequate supply of air, a very considerable proportion, to wit, from 15 to 35% of its weight, can be obtained in the form of Lamp Black by deposition in suitably arranged chambers.

The quality of the black is determined by the size and shape of the furnaces in which the oil is burned; by the heat to which it is subjected in the process of manufacture; by the position in which the black is deposited and by the care that is exercised in the process of manufacture and in the selection and preparation of the raw materials.

The oil is usually allowed to flow in a sluggish stream into an earthenware or iron pot or pan, in which it burns and from which the smoke passes through flues into the chambers in which it is deposited.

To absorb and utilize commercially some of the heat, boilers are often placed within reach of the flame and the steam thus generated is used for the industrial processes that may take place in the same factory. Care is necessary to entirely free from water whatever raw material may be employed and also to protect the reservoirs and the pipes from them to the burners from excessive cold in the wintertime, which might cause a stoppage by the coagulation of naphthalene and anthracene or other solid matter in the pipes. A screen is often used at the final exit from the black-condensing chambers in order to hold back the last traces of the black, both on account of its value and because the smoke that passes from a lamp black factory is very annoying to neighbors.

The best grades of black, generally speaking, are obtained in furnaces of moderate size, so built that the black is prac-



tically calcined at the time it is deposited and carries down with it but very little empyreumatic matter. The products of combustion are usually carried through a series of chambers and the black is assorted according to its distance from the point of origin, the lightest being that furthest from the flame and for this reason commands better prices for certain purposes.

These chambers are periodically emptied and before doing so, it is needful to be sure that the black is thoroughly cold and is not afire, for if too much oxygen comes into the chambers it sometimes happens that the black gets afire and the fire may lurk undetected unless great care be exercised. Generally speaking, an experienced workman can detect fire by the smell of the carbonic oxide and the workmen are thus put on their guard to hunt out and extinguish the fire. It sometimes happens the amount of carbonic oxide gas is dangerous to the workmen and this danger should be borne in mind. This gas is very poisonous.

It has been observed that the smokiness of a flame can be increased by artificial cooling, for instance, if you bring a coarse wire grating into an ordinary gas flame, it immediately begins to smoke and various attempts have been made to utilize this principle to increase the yield of Lamp Black, but so far as I know, the only practical application has been the generation of steam in boilers by the heat of the Lamp Black furnaces.

It is good practice to introduce partition walls in the chambers used for deposition, thereby increasing the distance that the products of combustion must travel before they finally escape in the open air, with a view to increasing the percentage of deposition, but this practice can easily be overdone, for if you divide up your chambers too much, you do more harm, by increasing the speed with which the products of combustion travel; than you do good by increasing the distance.

Mechanical devices have been used in the form of stirrers, which churn the air and cause the condensation of the smoke in masses sufficiently large for it to deposit itself. I do not know whether any of these devices are now in use on a commercial scale. The soot thus obtained contains in the neighborhood of 80% of carbon, the rest being chiefly oxygen and hydrogen, with traces of grit on the walls and floors of the collecting cham-

bers and a greater or less percentage of oil or other empyreumatic matter.

This oil or empyreumatic matter can be driven off by heating the black in sheet iron boxes, care being taken, on the one hand, to heat it sufficiently to drive off the oil, and on the other, not so hot as to affect the mixing strength and it is possible, as already stated, by a proper proportioning of the fireplace, flues and the supply of raw material and a proper arrangement of the temperature and other conditions, to cause a deposition of a certain amount of black practically free from empyreumatic matter from the start.

Resin, resinous woods, tar, pitch and other raw materials have been and still are, to a certain extent, used in the manufacture of Lamp Black, but generally speaking, the quality thus obtained is less good than that obtained from the dead oil of tar and other distillates and such inferior raw materials are comparatively unimportant as a commercial source of Lamp Black.

There is not time here to enter into the great variety of different shapes and sizes of ovens, collecting chambers, various devices for regulating and controlling the draft and the many different complications of detail that have been and are still used in this business.

Before passing on to Carbon Black, I will briefly mention the methods of making Lamp Black by the heating of hydrocarbon vapors out of contact with air. For a typical instance of this see Patent No. 866883, by Albert D. Purtle and Irving E. Rowland of Salem, W. Va., These gentlemen have described their patent as a process of making Carbon Black, but this is a misnomer, for the resulting pigment has nothing like the strength of Carbon Black obtained by the depositing process and in appearance and properties more nearly resembles the ordinary Lamp Black of commerce.

For years a similar process was used to extract carbon from natural gas to be used in the manufacture of electric light pencils near Red Bank in the Alleghany Valley, Pa., but the carbon thus obtained cost too much to compete in the long run with coke, which is now the chief raw material for these pencils. For some reason which I do not pretend to understand, Lamp Black thus

obtained is apt to contain particles of adamantine carbon, so hard that they will scratch glass.

Another commercial obstacle is the high cost of the apparatus and the large expense from deterioration as compared with the value of the finished product. Therefore, although a much larger proportion of carbon can be obtained from natural gas by this than by any other known process, all such efforts have, up to this time, failed to show a commercial profit, but I believe that this method of making Carbon Black will sometime be successfully applied.

Attempts have been made to first volatilize the raw material and secondly burn the resulting vapor on the smudge system with an insufficient supply of air and collect the resulting soot, but I do not know that any such attempts have proved profitable on a commercial scale. I should hardly think they would.

Various devices have been adopted to perfect the separation of the soot from the air and I may say that both in the manufacture of Lamp Black by the ordinary smudge process and in the manufacture of Carbon Black by the contact process, one of the most difficult problems is the proper separation of the black from the air in which it floats or which it holds mechanically when it settles.

In the case of the smudge process, are some times used adjustable blinds by which the black enters the chimney and which can be worked just like the adjustable slats on an ordinary window-blind, although they are best made of iron. Thus the draft is regulated and eddies are formed which help to cause the black to unite in larger pieces and settle out.

High pressure electric discharges of a static machine have been used experimentally for causing this separation of the black from the air, but this is too expensive and cumbersome a method to have proved profitable on a commercial scale, and, of course, on a large scale high pressure discharges are dangerous. The best material for the chambers in which the black settles, is masonry with cement floors and a brick roof put together with cement mortar.

When a new plant is put in operation, the black first made is apt to contain moisture, condensed by the coldness of the walls;



empyreumatic matter which has not been calcined out for the same reason, and grit, which at first comes off the walls to an annoying extent, even when great care is exercised in construection. This black is sold, usually at a cheap price, to those who are willing to use a black containing grit and only after the operation has been carried on for some time, so that everything is warm and in good running order and the loose grit has fallen, can the best results as to quality be obtained.

The Lamp Black which is thus precipitated, can be freed from empyreumatic matter by calcining, as already stated, or by washing with alkali or acid. So far as I know, there is practically none of it ever washed with alkali or acid, the expense of drying being very material and in general, the handling of black is a difficult and expensive process, owing to its great bulk and extreme lightness, which means a great deal of loss and much dirt and disagreeable work, and it is more and more the aim of lamp black manufacturers to so conduct their process that the black is calcined in the process of making, at least, to an extent satisfactory to most buyers.

In the case of Carbon Black, the black when first scraped from the plates is so light that 30 pounds will fill a sugar barrel. When you consider that the specific gravity of Carbon Black is about 1.7 (that is, very much heavier than water) you will perceive that 95% of the bulk of black as it comes from the plates is air and the problem of packing is to separate this black from the air so far as is commercially feasible.

This can be done by screw-packers, similar to those used for packing flour, but different in detail and run at a very much lower rate of speed, or it can be done by a plunger, lined with sheep-skin, the wool side out, worked up and down vertically by a ratchet or screw.

An essential element is time. You cannot hurry the process of packing Carbon Black without much loss by spurting of the black through the air and many other evils not needful here to mention.

As it comes into the market, a sugar barrel will hold from 75 to 80 pounds. In fact, we get 80 lbs. into a barrel of less than sugar barrel size; which means that the black has been compressed

to about one-third of its original bulk and that about 88% of its bulk is still air. Under these conditions, it is very hard and many buyers insist on its being less hard pressed, owing to the greater difficulty of grinding, but its ultimate quality for most uses is not affected by this pressure.

In Koehler's book on the Manufacture of Black, are mentioned four different firms that at one time had factories for the manufacture of contact black from oil, using for this purpose a heavy mineral oil burned in burners beneath a plate on the upper surface of which was water and around the rim below a shield to protect the burners from side-draft.

The capacity of these factories, if I correctly understand this article, would be about 170,000 pounds a year, but I do not think anywhere near this amount was ever made. The apparatus was very expensive in proportion to the output and the price at which the black was sold forbade direct competition with American natural gas black, of which probably more is made in a day than was ever made of this other black in a year.

The raw material used in this European process was a heavy shale oil and I believe in actual practice they volatilized it and scrubbed the gas to remove the impurities.

There is still another source of Lamp Black, to wit, Acetylene Gas, obtained from the refuse of Carbide of Calcium factories, namely, those grades of Carbide of Calcium, containing too small an amount to be merchantable.

This acetylene gas possesses the remarkable quality of exploding by itself alone without the admixture of air and Jaenecke & Schneemann were in the habit of making black by exploding it under 5 atmospheres, either by compression or by an electric spark.

The great trouble is, first, that it is very hard on the apparatus and second, a black thus obtained is very inferior in color and strength to Carbon Blacks from natural gas. It is essentially a by-product; the supply is very uncertain and the price very irregular, but always averages very much higher than that of Carbon Black. Therefore, it can only be used where its bluish tinge gives it the preference in certain trades.

Carbon Black is the trade name given in this country, and to

a certain extent abroad, to Lamp Black made upon the surfaces of metal or stone by direct impact of flame.

The first Carbon Black ever made in this country and sold in a commercial way seems to have been made in the year 1864 by J. K. Wright, an ink maker of Philadelphia, Pa., for use in printing ink.

This industry is, therefore, a comparatively new one in this country, and it certainly never attained any great importance abroad, although I cannot say when it was first made in other countries. Mr. Wright made Black on sheet iron cylinders revolved over gas jets, from which the Black was removed by stationary scrapers. This process was used by other ink makers for making Carbon Black from artificial gas in a small way for use in printing ink, and a very glossy, high-priced ink, of intense color, was obtained.

These pioneers in the Carbon Black industry apparently did not consider the process of sufficient importance to patent it, for the first patent granted in this country was issued Dec. 10th. 1867, to A. Millochan, New York, for a process which proved to be of no value, and it was not until the year 1872 that any process was patented that was subsequently used on a regular commercial scale. It had attracted the attention of many different people, among others, Peter Neff, Gambier, Ohio, and John Howarth, Salem, Mass., that large quantities of natural gas going to waste in the gas regions offered a cheap and abundant raw material for this manufacture, and on Sept. 17th, 1872, John Howarth received a patent for the manufacture of Carbon Black from Natural Carbureted Hydrogen Gas, claiming the production of Carbon Black from a natural carbureted hydrogen gas issuing from the earth, etc. His plan was to connect the gas well with a gas-holder, such as is used in artificial gas works, and with a blow-off from which might escape the surplus flow of the well not required in the process of manufacture. As the natural pressure of gas in the rock sometimes exceeds five hundred pounds on the horizon from which he derived the supply of his factory and there was at that time no method of regulating the flow, this waste of gas was a necessary feature of his enterprise. From the gas-holder, the gas passed through pipe to ordinary gas jets



arranged in the same horizontal plane beneath slabs of soapstone. These slabs of soapstone were provided with holes for ventilating, without which the carbonic acid gas, and other inert products of combustion, would have formed a layer about the middle of the slabs and kept the flame away from the surface, thereby diminishing the yield and impairing the color of the resulting product. Above these slabs of soapstone rose, in an arch, an iron dome or hood with a chimney at the top of this arch, and in this chimney a damper that could be set to give the right amount of draft. On the slabs rested pans of water closed in and kept cool by a continuous circulation. The edges of this arch descended below the edges of the soapstone slabs and were grooved longitudinally with horizontal grooves in which ran a scraper that could be pulled to and fro by hand with a long handle. This scraper removed, from time to time, the deposited soot which fell into the sheet iron aprons or troughs which hung from the burner pipe. From these again the Black fell through discharge pipes into receptacles which could be changed by hand when full. This was a very crude, clumsy and expensive way of making Carbon Black, decidedly less advantageous than that previously employed in making Black from artificial gas, but, nevertheless, owing to the cheapness of the raw material, the price, which had been \$3.00 to \$5.00, was immediately dropped to \$2.50, and then to \$1.50, and shortly after to \$1.25 per pound. It is, however, a curious fact that the Black from natural gas does not possess all the qualities of that made from artificial gas.

The next patent granted for Carbon Black was for a cylinder cooled externally by water and slowly revolving over burners placed on its interior, but I am not aware that this process was ever used.

On March 23rd, 1875, John Howarth received a further patent on a travelling car which hung from rails running length-wise of the bench or row of slabs, and these rails also held between them the slabs themselves. This car carried a scraper, a shallow frame, and, hanging to that frame on each side, two deep receptacles of sheet iron which could be detached at will and emptied. These receptacles were joined together over the burners by a narrow arch of sheet iron, just wide enough to allow

the apparatus to pass over the single row of burners without striking. The car was drawn by an endless rope passing over pulleys and pulled first in one direction and then the reverse. The scrapers were held against the plates by wire springs and were only in contact with the plate when passing toward the end at which the receptacles were removed. The dome was a superfluous adjunct. Cast-iron was better than soapstone and there was no need of water cooling. Indeed, Mr. Howarth never used water cooling on a commercial scale. Obviously, its effect would hardly be felt through such a non-conductor as soapstone.

The first factory was located at New Cumberland, West Virginia, and the gas came from what is known as the salt sand, and was very rich in carbon and made an excellent Black. The factory was made of wood and before long it burned down and the business was removed to Saxonburg Station, Pennsylvania. In two or three years, competition sprang up at Gambier, Ohio, where a small factory was erected by Mr. Peter Neff, who made Black by a somewhat similar process for something like ten or twelve years. He had as many patents for Carbon Black apparatus as all the other inventors put together, or thereabout, but most of them were fantastic and useless. His factory reached an output at one time, of 125 pounds per day.

The next important competition was by a Mr. A. V. Nolen, who, in the year 1879, built a factory at New Cumberland, West Virginia, and made Black on cast iron pans holding water. By this time the price of Black had gone down to about 60 cts. per pound, but nevertheless where the two pioneers had met with little pecuniary success, Mr. Nolen, by superior ability, made a good deal of money, and bought out the original company. Various other small factories were started from time to time, but it was not until the year 1883 that any considerable advance was made, when the firm of L. Martin & Co., of Philadelphia, became interested in a small and struggling enterprise at Foster's Mills, Pennsylvania, and there erected five plates 24 feet in diameter, cast in segments and suspended on a central mast which rotated with it upon a bronze bed plate. Beneath this was fixed a stationary burner of parallel, horizontal iron pipe, 1 1-4"

in diameter, branching from a central supply 3 3-4" inside diameter, and this, in turn, connected suitably with the well.

Incredible as it may seem, even at this time, after ten years of experience, no attempt had been made by either of these three leading manufacturers to control the flow of gas from the wells, although this was then quite possible with available appliances, and a blazing torch at each gas well, wasting daily millions of feet, was a feature at the principal factories, including that at Foster's Mills, Pa. About the same time a factory was started by Samuel Cabot in the adjacent village of Worthington, at which some efforts were made to confine and economize the gas, but it remained in large part fruitless for some years, owing to the inefficiency of the foreman. At the factory at Foster's Mills, the idea of a travelling box and scraper was discarded and a plan for the first time successfully adopted on a commercial scale of a horizontally rotated collecting surface. The same principle was adopted at Worthington at about the same time, but failed of success owing to purely mechanical imperfections. At first blush, it would seem as if the original idea of moving only the scraper box was the correct principle, and yet it is now entirely abandoned, and about two-thirds of all the Black that is made today is made on surfaces which are moved over a stationary scraper box and stationary burners.

The first decade of the manufacture of Carbon Black from natural gas on a commercial scale was the epoch of factories in which the collecting surfaces were arranged in rectangular shapes, placed end to end to form what the workmen call "benches."

The details whereby the Black was collected, the dimensions of the different parts and the arrangements of the size of the burners varied in different factories; but four-fifths of all the Black made was made on benches, and the rest was made on the external surfaces of rotating cylinders. Various efforts were made to use petroleum oil and the firm of Carnahan & Swan, of Duke's Center, Pennsylvania, made a very fine Black by this method for several years.

Various other manufacturers of Carbon Black tried to use oil, and were tempted thereto by the greater amount of Black deposited by a flame of a given size on a given surface; but one and



all of them found it unprofitable, owing to the great expense of oil and the danger of fire, which increased very greatly with any increase in the size of the apparatus. An apparatus which worked perfectly well on a laboratory scale was quite unsafe on a commercial scale. At the end of this epoch, Mr. A. V. Nolen was the largest manufacturer and the total output was probably ten hundred to fifteen hundred pounds a day. The year 1883 brought with it the introduction of large rotating plates, which replaced at Foster's Mills, a factory in which benches had been used. A scraper box and scraper was placed radially so that in revolving the scrapers were at right angles to the direction in which the surfaces passed across them. The Black was removed by a screw conveyor in the bottom of the scraper box which carried it outward to a longer conveyor which ran tangential to five plates in a row and carried the Black to a rotating bolt through which it went into the bin. It was then lifted from the bin by hand in large scoops and packed by hand with a screw press, but the Black is very light and the handling of it was very dirty, unhealthy work, involving considerable loss in raw material. In the earlier factories it had been the habit to brush the Black through a fine horizontal sieve by means of brushes rotating on a vertical axis. A bolt revolving on a horizontal axis which discharged the coarser particles of Black at one end and allowed only the finer particles to fall through it, was a decided improvement. In the same year, a very able young man, named A. R. Blood, of Warren, Pennsylvania, devised a method in which a small plate about 3 feet in diameter was used. The advantage of this was that no ventilation holes were needed, as in the case of the larger plates, excepting, however, that this small plate was cast in the form of a ring with an opening in the center. This plate was moved by means of a ratchet at the center. This ratchet was worked by a lever, and this by another lever revolved on a shaft. Every time the shaft came around it would give the plate a little shove which would move it 1 1-2 inches. Beneath the plate was a scraper in the mouth of a radial hopper, through which the Black fell into a longitudinal conveyor running beneath the row of plates. There were sixteen plates in a row and five rows in the building. The building was of sheet iron on a

framework of pipe and angle iron and was pierced with small holes near the bottom to give the needful supply of air. Along the ridge pole was an opening about 30'' wide and about 6'' above this, a little pent roof, to prevent the entrance of rain. The space between was something like 6'' through which the products of combustion passed. All of these factories used gas jets either of iron or steatite, such as are ordinarily used in houses. There was one factory which used Argand burners but it did not last many years. About this same year 1883, E. R. Blood, the father of this A. R. Blood, began making Black on the roller process, and using a burner with a small hole in the point of the tip giving a round flame. This Black was at first very unprofitable owing to the small yield and comparatively poor color, but the successors of Mr. A. R. Blood improved the details of manufacturing and experience has shown this Black to possess some valuable qualities and in spite of its inferior color it sells for a high price and is very profitable to the owners, the Peerless Carbon Black Co., of Pittsburg.

This company was for many years the only company making Carbon Black in this country from natural gas on revolving cylinders, although in earlier days there were two or three factories on this principle, and are now three such factories.

In the second decade the process of making Carbon Black introduced by Mr. A. R. Blood became the most important as to output and total value of Black produced. The prices of Black fell rapidly and reached 7 cts. per pound by the year 1887 and 4 cts. per pound by 1889. After this there was a considerable improvement in prices, followed by a further rapid increase in output and by the close of the second decade the total output had reached about 10,000 pounds per day, worth at that time about 6 cts. per pound on an average. Toward the end of the second decade two new processes began to become an appreciable factor in the total output. The first of these was our process whereby, under 24 foot plates, similar to those previously mentioned, though varying somewhat in details, was rotated a burner and black box radially placed. The burner was made up of parallel 1 1-4'' pipe inserted in a central supply pipe 3 3-4'' diameter. As first used the radial black box discharged into

a hopper placed at the side of the plate by means of a little trap door with a lever which was pressed in such a way as to open the trap door every time it passed over the hopper and after the discharge the trap door closed again by means of a counterpoise. This method of a rotating burner was introduced at Worthington somewhere about the year 1884, but did not become a commercial success until the year 1887. The factory changed hands and the new owner changed the method to that of a central discharge whereby the Black was continuously discharged downward by a vertical spout at the inner end of the radial black box into a circular ring-shaped box; thence it went through a hole in the bottom into a long conveyor. By the former method, the long conveyor had been tangent to the ring and by this it went within two feet of the center. A cover was hung above this round box in such a way as to exclude air and rotate with the burners, black collecting box, etc. The bottom of the vertical spout above alluded to pushed the black in front as it slowly swung around the ring until it reached the orifice through which the Black fell. One great advantage of this method was that the Black was not exposed to the air. By the former method whenever the box emptied, a cloud of Black arose, making a nuisance and a great loss of output. As rebuilt, the Black was kept under cover and carried to a bolt, also shut in, and raised from beneath this bolt in an elevator into a bin. From this bin, it was packed by machinery in either sacks or barrels, always under cover, so that from the time the Black was made until it was used by the consumer, it was never touched by hand and was always under cover and protected from all appreciable drafts of air.

The other process above referred to was introduced about the year 1891 at a place called Gallagher, Pennsylvania, and consisted of a system of channel beams turned with flat side downward over horizontal rows of stationary burners and black boxes. By a reciprocating mechanism, these beams slowly moved back and forth and the Black was scraped and removed by a screw conveyor in the usual manner. This Black was packed direct without bolting.

The chief advantage of this system is the perfection of the surfaces, which are smoother than the surfaces of cast-iron plates.

In the beginning of the third decade of this industry, another attempt was made to manufacture Carbon Black with the help of petroleum and under a somewhat new principle by evaporating petroleum and burning its vapor through gas burners. The cost of making this Black was probably less than that of any other Black made from petroleum by the contact process; still more than could be realized by its sale. One great difficulty was the formation of adamantine carbon in the Black. These particles were so hard that they would scratch glass and the manufacturer was unable to discover a method of removing them. Since that time there has been no Carbon Black made from oil on a commercial scale in this country, although there is a small amount of a very expensive grade made in Europe from what are known as gas oils, a heavy oil obtained in the distillation of shale and chiefly used by manufacturers of illuminating gas. No important improvement in Carbon Black making appeared in the third decade. The output steadily increased and reached 20,000 pounds a day.

The price fluctuated a good deal, the average for the decade (1893-1902) being about 6 cts. The amount of Black produced with rotating burners and with the reciprocating channel beams very considerably increased. There were also modifications made in the process of the small stationary plate, and the amount made on this general principle increased. In 1902, about one-quarter of all the Carbon Black was made with rotating burners; and something like one-fifth with reciprocating channel beams; not quite one-half on rotating cast-iron plates, mostly with the smaller sizes; and the rest chiefly with rollers. There was only one factory in existence which operated on the bench principle.

In the year 1899, the construction at the Grantsville factory was begun, operating on the principle of 24 foot plates, with revolving burners and black-box, etc., beneath them.

By the end of the third decade, namely, about the year 1902, this had become the largest factory in existence and has since been still further increased until it is making about 10,000 pounds a day. Possibly a brief description of this factory may be of interest.

It lies on the right bank of the Little Kanawha River and com-



prises 113 plates, each 24 ft. in diameter and surrounded by protecting rings of corrugated iron, 26 ft. in diameter. Above these plates is a roof made partly of diagonal sheets of sheet iron and partly of rectangular sheets of corrugated iron and reaching about two-thirds of the way to the top of the 16 ft. mast on which these plates are hung, leaving, therefore, in the center a space having about one-third the diameter of the plate, through which the products of combustion can escape upward.

These plates are arranged in rows about parallel to the river and disposed on two side of a central avenue which runs from the river to the road, at right angles to both.

The Black is collected by long conveyors running through the center of the rows of plates, toward the central avenue, where it passes into larger conveyors, which bring it to the packing-house; elevate it into bins and from them the black is packed partly by sack packers and partly by barrel packers, which work with a plunger.

The black is carried down the Little Kanawha River in gasoline boats whenever there is water in the river. Large tanks, containing about a thousand barrels of water, stand on the hill-side above the factory and the factory is adequately piped in every part over an area of about 6 acres, whereby water can be turned on, either for the purpose of putting out fire or for the purpose of knocking black out of the ventilator holes in the rings on which the black is deposited.

These rings are of two patterns,—one of them made with 14 radial arms in the shape of T-rails, which support 70 cast iron plates, 5 between each pair of arms. The other pattern has for each plate 48 segments, 16 in the inner row and 32 in the outer row, which are supported directly by guys. In each case the plate is supported by guys which are screwed into a cap, which has approximately the shape of a very blunt, truncated cone. This cap rests upon the top of the hollow mast and the joint between the cap and the mast is made good with asbestos board.

The mast stands in a bed-plate on the upper surface of which is a groove, in which run  $1\frac{1}{2}$ " steel balls. Upon these steel balls rests a casting, having 8 horns, projecting outward and upward and fixed in the lower ends of struts made of 2" pipe. On the

outer end of these struts of 2" pipe, is an angle-casting into which the 2" pipe fits and through which a horizontal hole accommodates a horizontal guy-rod, attached at the inner end to an octagonal plate, which rotates with the burner around the central mast.

On the outer end of these horizontal guy-rods, are 3-4" nuts, and by screwing these up, the struts can be raised to the correct position, thus regulating the height of the burners beneath the plate. On the face of these angle-castings, supported by the 2" struts, is bolted an iron-bar, hanging vertically down from these angle-castings and to this iron-bar is attached an angle iron, in which runs the chain that rotates the burners, black-box, etc.

Against these angle-castings is also bolted a horizontal ring, made of bars  $4\frac{1}{4}$ " x 1-4", forming a circle around the plate and on this ring is supported the grid-iron of burner pipe. This grid-iron of burner pipe has as its central supply a piece of 3 3-4" casing, 22 ft. 6" long, and this casing, in its turn, is fed with gas by  $21\frac{1}{2}$ " pipes, connected with the help of 4 ells and a union to an octagonal gas-box, at the top and bottom of which sit glands. This gas-box is fed through holes in the mast. The glands are stuffed with asbestos so that the gas cannot escape as the black-box revolves around the mast.

I have mentioned at an earlier period in this paper that the black is removed from the plates by scrapers, placed radially to the mast above a black-box, in the bottom of which lies a screw conveyor, which in its turn is actuated by a pinion, on its inner end, which engages a bevel fixed to the central mast. Beneath the octagonal plate, to which the horizontal guys are fastened, is bolted a hanger in which turns the shaft of the conveyor which carries the pinion just mentioned.

On the inner end of this black-box, the black descends in a vertical 3" pipe through the rotating cover into the circular box from which it discharges downward into the long conveyor, which runs tangent to this circular box and two feet from the center of the ring.

In the last decade the factories in Pennsylvania have all of them been moved to West Virginia, with three unimportant exceptions, to wit, two factories not in use and the third, a factory producing only 50 lbs. a day.

A new factory has been started in Oklahoma and the total output of Carbon Black has risen to about 65,000 lbs. a day. Certain new processes have come into use which are, however, only modifications of those previously mentioned. In one factory, namely, that of the Bristol Oil & Gas Co., the black is collected on a hollow channel iron, flat beneath, and through which a blast of air is blown, with a view of cooling the plates.

The question is often asked whether the heat of the gas used in the manufacture of Carbon Black is saved or lost and why. It is always lost and for the reason that the expense of utilizing this heat would greatly exceed the value of the power to be obtained. Our Grantsville Works, producing about 10,000 pounds of black a day, are operated by five gas engines, which probably do not consume fifty cents worth of gas a day at the price which I am paying for gas.

If these works were in the immediate vicinity of a large city, it is probable that it would pay to circulate water underneath them in an immense coil and heat the neighboring quarter of the city with hot water. Located as they are in a sparsely settled country, 30 miles from our railroad terminus, there is no practical way of saving this heat. Wasteful as this operation seems, it is better than that all of this gas or a great part of it, should pass into the atmosphere through the numerous oil wells of the Yellow Creek and other adjoining fields. A much larger quantity of gas has been wasted than all that we have consumed in the Little Kanawha Valley since we have been there.

Another source of waste in this manufacture is the smoke, which ascends day and night to a very great height in the atmosphere and can sometimes be seen at a distance of 18 miles, but this consists of a lamp black, rather than Carbon Black and would probably only sell for two or three cents a pound if it could be collected and the task of collecting, even one-half of it, would probably be much more expensive than the whole maintenance of the factory and its fuel supply.

I have personally no doubt that great economies are possible and would not for one moment wish to convey the impression that the Grantsville factory or any factory now in existence, is the last word, but at the same time, they are the result of many

hundreds of experiments by myself and others and we still peg away, trying every year to learn something and make some improvement and it is to me surprising that considering all of the thought that has been given to the matters involved, so little progress has been made in the last twenty years.

The total value of Carbon Black made in a year would somewhat exceed one million (\$1,000,000.) dollars and the total value of the world's output of Lamp Black would probably be two or three times as much, but the real importance of these two commodities to humanity is inadequately represented by these figures.

They form the basis of the black printing inks, with which all of our printing is done and are also largely used in black paints, stove polish; for coloring rubber, oil cloth, leather and many other substances too numerous to mention.

It is rather a curious fact that the uses of Carbon Black and Lamp Black are separately defined and quite sharply defined at that, so that the market price of each commodity fluctuates with little reference to the market price of the other.

Carbon Black is much better for black ink, stove polish, vulcanized rubber. Lamp Black is much better for coloring oil cloth, leather and other forms of rubber and is much more widely used in paint, although Carbon Black is better for certain kinds of paint and varnish.

Generally speaking, if a buyer is using a black made on the smudge process, or by the heating or explosion of hydrocarbon vapors, he does not wish to change and take the black made on the contact process, and if a buyer is using a black made on the contact process, he cannot safely switch over onto a black made on the smudge process or the explosion process.

The gradual diminution of the margin between the cost of making black and the average selling price goes on and there seems to be no reason why it shouldn't continue through the present decade. There seems no likelihood of any shortage of Carbon Black, excepting from some temporary cause, or any great and permanent enhancement in the price during the life of any one now living.





## THE RARER PAINT OILS

BY HENRY A. GARDNER

*Assistant Director, The Institute of Industrial Research, Washington, D. C.*

On account of its present scarcity, linseed oil might be classed as the most prominent of the so-called rarer paint oils. The subject of this paper, however, is meant to include only those oils which have been under test or which have come into general use to make up for the shortage of linseed oil. This paper will not go into the chemistry of the oils considered, as it is based upon a series of empirical tests primarily intended to afford to the paint grinder definite information as to the relative suitability and durability of certain oils as constituents of paint vehicles.

Among the newer oils, the one used to the greatest extent is that produced from the soya bean, a legume grown in Manchuria for its oil content and food value. Although the soya bean has been grown extensively in America as a forage crop, it is only within the last year or two that it has been cultivated in this country as a source for paint oil. Quantities of soya beans have recently been crushed by the cottonseed mills in several of the Southern States, and American grown soya oil is now available to the trade. Whether this oil will be used as a source for soap stock or for paint oil, is a question which will ultimately be determined by the cost and quantity produced. On account of its iodine value, which is much lower than that of linseed oil, soya oil has been classed as a semi-drying oil. From the standpoint of actual drying, however, it is a much better paint oil than other semi-drying oils of like iodine value. Probably its first application in the paint industry was in admixture with linseed oil, in the grinding of colors. Some manufacturers claim that certain pigments are less liable to harden in the package when ground in an oil mixture containing soya oil than with straight linseed oil. Later on soya oil was admixed in quantities up to

about 25% with linseed oil, and used in the manufacture of general mixed paints. There is no doubt but that some manufacturers have used it to a greater extent, but the mixture based upon the above percentage has been the one most favored, showing constants similar to La Plata and some other pure linseed oils. It has been stated that of the various types of soya beans which are grown, only a few yield an oil which is suitable for paint making purposes. Many authorities, however, are inclined to doubt this statement, as practical tests upon several types of oil produced from various varieties of beans, have shown good results. The importance of using a rapid drier with some grades of soya oil, has, however, been shown by Toch.<sup>1</sup> Very recently heat treated and bodied soya oils have come into the market. These oils have been subjected to high temperatures in the presence of driers and with the introduction of air. Such treatment not only raises the gravity and the general drying properties of the oil, but, at the same time, lightens its color and makes it more suitable for use in paint. Some very important heat treatment tests on soya oil are now being conducted by sub-committee C on Paint Vehicles, of the American Society for Testing Materials. The object of these tests is to set up standards that may be used in determining the quality of various samples of soya oil offered to the trade.

Perilla oil, which in chemical constants, color, drying and general properties is similar to linseed oil, has never been imported in sufficient quantities to come into general use. It should, however, find favor among the trade, and it will undoubtedly become one of the newer oils to be used in the general manufacture of paints and varnishes.

Menhaden oil has been so refined as to become of fairly good odor and of a color even lighter than linseed oil. Its rapid drying and ability to form a waterproof film well fit it for use in many technical paints, and especially for marine compounds. In combination with linseed oil paint designed for the protection of exterior wooden surfaces, it has shown good weather resisting properties. Its most prominent defect is that of taking dust and becoming dark. These latter features are shown to some extent

<sup>1</sup> New Paint Materials. Proc. Paint & Varin. Soc., London, May 1911.

by all marine animal oils, and probably to the greatest extent by whale oil, one of the newer oils which was recently proposed as a partial substitute for linseed oil.

Corn oil and cottonseed oil are both very slow drying oils, and recent attempts to heat treat them in the presence of a current of air and drier failed to accelerate their drying character materially. When either of these oils are ground into paint and applied to wood, the film remains rather tacky for a long time, and prone to take dust. This slow setting is, however, said to be beneficial, as the film generally remains very elastic and less subject to the checking that is sometimes shown by very rapid drying oils.

Chinese wood oil has already found its place in the paint and varnish world, having become a most important constituent of several of the highest grade varnishes, enamels, floor paints etc. This statement refers to wood oil that has been heat treated (boiled with litharge and resinates) to overcome the opaque, crystalline character of film with which the raw oil dries. The ability of the treated Chinese wood oil to dry to a film of high gloss and great hardness, has well fitted it for the protection of cement and concrete surfaces. For the protection of iron and steel, paints are now upon the market, containing small percentages of treated Chinese wood oil in combination with linseed oil. So far these paints have given excellent results. The rosin content of treated wood oil is, however, apt to cause checking when it is used to any extent in paints for the protection of wooden surfaces.

Rosin oil and mineral oil have places of their own in certain grades of paint, but their use in the highest grade paints for the protection of wood should be discouraged.

The writer has made several interesting exposure tests with wooden panels painted with paints made up with various percentages of the rarer paint oils. These tests have already thrown considerable light upon the wearing of such oils, and will in the future afford further information of a reliable nature. The first series of tests made were at Nashville, Tenn., upon a test fence especially designed for paint exposures. The second series of tests, which is probably the most comprehensive series of practical paint vehicle tests ever made, is at Washington, D. C. A brief



description of these tests, together with a report upon their condition, is given herewith.

*Nashville, Tennessee, Test Fence*

Panels painted in August, 1910. Exposed in September, 1910.  
Inspected February, 1912.

Pigment Formula Used in Tests

|                               |       |
|-------------------------------|-------|
| Corroded White Lead . . . . . | 45%   |
| Zinc Oxide . . . . .          | 45%   |
| Asbestine . . . . .           | 5%    |
| Calcium Carbonate . . . . .   | 5%    |
|                               | <hr/> |
|                               | 100%  |

Test No. 38 Vehicle Formula: 50% Linseed Oil  
50% Soya Oil

Chalking: Medium

Checking: Very slight

General Condition: Very good

Remarks: Darker than Test No. 31 (the above pigment formula ground in pure linseed oil)

When applied, the drying was slightly less than with Formula No. 31 in which 100% of pure linseed oil was used. The film is in very good condition and the surface is very slightly darker than Panel No. 31.

Test No. 39 Vehicle Formula: 50% Linseed Oil  
50% Corn Oil

Chalking: Medium

Checking: Very slight

General Condition: Good

Remarks: Darker than No. 31 and softer

When applied, 10 days time was required for drying between coats. The film is rather soft to the touch and is much darker than No. 31 or No. 38, on account of adhering dust.

Test No. 40 Vehicle Formula: 50% Linseed Oil  
50% Cottonseed Oil

Chalking: Medium

Checking: Very slight

General Condition: Good

Remarks: Darker than No. 31 and softer

Similar to No. 38.

Test No. 41 Vehicle formula: 50% Linseed Oil  
50% Rosin Oil

Entirely disintegrated.

When applied, it dried slowly, with a yellowish color which later on was bleached white by the sun. Rapid chalking followed, and alligating soon appeared, accompanied by a partial return to the yellowish tint observed at the start of the test. Cracking and scaling has removed most of the paint.

Test No. 42 Vehicle formula: 50% Linseed Oil  
50% Pine Oil

Chalking: Considerable

Checking: Considerable lateral checking. Tendency to scale

General Condition: Fair

Remarks: Quite white

Dried rapidly, when applied, to a semi-flat surface of great whiteness. Probably used in too large percentage for efficient results.

### *Washington Test Fence*

Painted in April, 1911, and exposed in May, 1911. Inspected May, 1912.

### Pigment formula used

|                                 |     |
|---------------------------------|-----|
| Basic carbonate-white lead..... | 20% |
| Basic sulphate-white lead.....  | 30% |
| Zinc Oxide.....                 | 35% |
| Magnesium silicate.....         | 10% |
| Barytes.....                    | 5%  |

Test No. 1 Vehicle formula: 100% Raw Linseed Oil

Chalking: Very slight

Checking: None

General Condition: Excellent

Remarks: Paint is very white and in excellent condition.

Test No. 2 Vehicle formula: 100% Soya Bean Oil

Chalking: Very slight

Checking: Fine matt checking evident in a few places

General Condition: Very good

Remarks: Panel is slightly darker than No. 1

Test No. 3 Vehicle Formula: 100% Menhaden Oil

Chalking: Very slight

Checking: None

General Condition: Very good

Remarks: Panel very dark. Color noticeable from distance.

Test No. 8 Vehicle formula: 50% Raw Linseed Oil

50% Blown Linseed Oil

Chalking: Considerable

Checking: Evident in a few places. Of fine lateral order.

General Condition: Good

Remarks: Panel has an excellent gloss and resembles an enamel.  
The paint is very white in appearance.

Test No. 10 Vehicle formula: 50% Raw Linseed Oil

50% Soya Bean Oil

Chalking: Medium

Checking: Very slight and of lateral order

General Condition: Good

Test No. 11 Vehicle formula: 50% Raw Linseed Oil

50% Menhaden Oil

Chalking: Medium

Checking: None

General Condition: Very good

Remarks: Panel slightly dark.

Test No. 12      Vehicle formula:      50% Raw Linseed Oil  
50% Perilla Oil

Chalking: Considerable

Checking: None

General Condition: Very good

Remarks: Panel Very white

Test No. 13      Vehicle formula:      50% Raw Linseed Oil  
50% Treated Chinese Wood  
Oil

Chalking: Very slight

Checking: Considerable checking of a lateral order shown

General Condition: Good

Remarks: Panel has a high gloss and is very white

Test No. 14      Vehicle formula:      50% Raw Linseed Oil  
50% Corn Oil

Chalking: Medium

Checking: None

General Condition: Very good

Remarks: Fairly dark

Test No. 15      Vehicle formula:      50% Raw Linseed Oil  
50% Cottonseed Oil

Chalking: Medium

Checking: Some lateral checking shown

General Condition: Good

Remarks: Panel very dark

Test No. 16      Vehicle formula:      50% Raw Linseed Oil  
50% Rosin Oil

Paint has turned very white and is showing alligating over the entire surface, with large scales of paint coming off in spots.

Test No. 17      Vehicle formula:      50% Raw Linseed Oil  
50% Whale Oil

Chalking: Very heavy

Checking: Slight and of a fine matt order

General Condition: Fairly good

Remarks: Panel has turned very dark. It is probably the darkest on the fence.





# WOOD TURPENTINES—THEIR ANALYSIS, REFINING, COMPOSITION AND PROPERTIES

BY L. F. HAWLEY  
*Madison, Wisconsin*

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## ACKNOWLEDGMENTS

It is with pleasure that the writer makes the following acknowledgments of aid received in this work:

The investigation was carried on in coöperation with the University of Wisconsin which furnished accommodations for all the work.

The Yellow Pine Manufacturers Association contributed funds toward the purchase of the refining still.

The crude turpentines used in the refining experiments were furnished through the coöperation of the respective producers.

Mr. Ernest Bateman, Chemist in Forest Products, collaborated in the development of the analytical methods and analyzed some of the products of the refining.

Mr. F. E. Lichtenthaeler, formerly Assistant Chemist, did most of the work in connection with the installation of the refining apparatus.

# WOOD TURPENTINES—THEIR ANALYSIS, REFINING, AND COMPOSITION

## INTRODUCTION

This investigation is a part of the general study by the Forest Service of the wood-using industries for the purpose of promoting the more economical utilization of the forest and its products. Crude wood turpentine is one of the important products obtained by most of the chemical industries using waste resinous wood as a raw material. The commercial turpentines prepared by the refining of such crude wood turpentines have been on the market for several years but there has been a general lack of authentic information on these products especially on the relations existing between the methods of production, the composition, and the properties; there was also no simple method available for the examination of these products by means of which the differences in their composition could be determined. A strong prejudice had also developed against any product sold under the name of wood turpentine, due partly to the large variation in the products from different plants and to the marked difference in odor between most of the wood turpentines and the commonly used "gum" turpentine, but aided also by the general lack of information on the subject.

These conditions have naturally resulted in a poor market for wood turpentines with a correspondingly slow development of the industry and incomplete utilization of the various kinds of waste wood available for the purpose. It was for the purpose of improving these conditions that this investigation was undertaken.

The following results have been obtained up to the present time:

1. A distillation method for the examination of turpentines has been developed from the results of which more complete and accurate conclusions can be drawn in regard to the composition of a turpentine than was possible from former methods of equal simplicity.

2. Five samples of crude wood turpentine produced by as many different commercial processes have been refined and methods of refining applicable to wood turpentines of a wide range in composition have been described.

3. It has been shown how the composition of wood turpentines is influenced by different methods of production, by refining and by storage and how wood turpentines compare with gum turpentines in composition.

The details of these results and the methods by which they were obtained are given in the following pages.

The next step in the investigation, the study of the relations between composition and industrial value, has been begun but since it will be sometime before the results are complete they will be reserved for a future publication.

## METHOD OF ANALYSIS

### *Need for a New Method*

There was necessary in this work a method for the examination of the crude turpentines and the volatile products obtained from them which would fulfill the following requirements:

1. Show quantitatively the proportions of the main constituents of the material examined, especially of those constituents which were to be separated in the refining process.
2. Show every possible difference in composition between the various refined turpentines.
3. Be fairly simple and rapid in operation.

No method was available which fulfilled these conditions. The usual methods for the examination of turpentines apply only to the refined product (usually only to gum turpentines) and are intended only for the detection of adulterations. The method described in Forest Service Circular 152<sup>1</sup> most nearly fulfills these conditions because, instead of determining the properties of the turpentine as a whole, the turpentine is first frac-

<sup>1</sup> "The Analysis of Turpentine by Fractional Distillation with Steam," by W. C. Geer.

tionated by distillation with steam and the properties of the fractions are determined; some idea of the proportion of the various constituents could, therefore, be obtained.

After an analysis by this method, however, the composition of the turpentine could be expressed only in terms of "constituents uniform in composition" and "heavy residue" without the possibility of distinguishing between the different kinds of turpentine or of obtaining indications of the actual chemical constituents present. It was found also (See pages 56 to 59) that the separation of the main constituents of the turpentine by this method of distillation was so incomplete—especially in cases where comparatively large amounts of "heavy residue" were present,—that the quantitative expression of the composition of the turpentine, even in such general terms as "constituents uniform in composition" and "heavy residue," was not accurate. It was necessary therefore, to have for use in this investigation another method for the examination of turpentines and the method described below was accordingly developed and adopted.

### *Description of Method*

This method is the same in general principles as that described in Circular 152 but is modified in several details so as to make it simpler, more accurate, and more rapid.

#### *Fractional Distillation*

Five hundred grams of the turpentine to be analyzed are weighed in a round bottomed flask of about 1,000 cubic centimeter capacity; the flask is connected with a condenser by a Hempel column of the shape and size shown in Figure 1 in the top of which is placed a thermometer with the bulb reaching to within one inch of the beads. The flask is heated on a sand bath or a piece of asbestos board and, in order to keep the liquid boiling smoothly without bumping, a small flat coil of copper or nicked wire is laid on the bottom of the flask. If the room temperature is very low a shield of asbestos board around the flask may also be desirable. The distillation is carried on at a



maximum rate of two drops a second<sup>1</sup> and the distillate is caught in weighed flasks of about 100 cubic centimeter capacity. Neither the size of the fractions, that is, the amount of distillate to be caught in each separate flask, nor the amount of undistilled residue to be left in the distilling flask can be definitely specified since the proper amounts may vary with different kinds of turpentines. In general, however, the fractions may well be larger (10 to 12 per cent) when the temperature of the distillation is changing slowly and regularly but should be smaller (4 to 5 per cent) when the temperature is changing rapidly. It is also usually unnecessary to continue the distillation after a temperature of 180°C., (corrected) is reached because this temperature seems to be reached just as almost all of the turpentine materials are distilled over and just before the heavy oils begin to come over in large quantities. This is especially true in the case of wood turpentines. In the case of gum turpentines and some wood turpentines, however, especially those with a small amount of heavy oil, the turpentine materials are all distilled over before this temperature is attained.

There are many details of manipulation which can not be completely specified in a method of this kind, which is to be applied to materials of widely variable character. Ordinary intelligence and a little experience are, however, sufficient to indicate the proper variations in detail which are desirable in the distillation of different materials.

### *Examination of Fractions*

The weight of each fraction is determined and the percentage weights of each fraction and of the total combined fractions (See Table I) are then computed. The maximum boiling point

<sup>1</sup> A slower distillation of course gives a better fractionation and the maximum rate mentioned should never be exceeded; there should, moreover, be no tendency to hasten the distillation in order to save time, because the work of determining the amount and properties of the fractions can be carried out at the same time as the distillation. Indeed, a moderately rapid and experienced worker with all the apparatus handy can make the necessary determinations and computations and can record and plot the results on six or seven fractions while nine or ten are being distilled.

of each fraction is read from the thermometer at the top of the column and the specific gravity and index of refraction of each fraction and of the residue left in the flask are determined.

*Boiling Point.*—The boiling temperatures as read should be corrected (1) for the prevailing barometric pressure using the factor  $0.956^{\circ}$  for every millimeter difference from the normal  $760^{\text{mm}}$  and (2) for the emergent stem of the thermometer according to the following formula:<sup>1</sup> To the observed value of the boiling point,  $T$ , should be added the factor  $0.000143(T-t)N$ , in which  $t$  is the temperature of the thermometer stem above the cork and  $N$  the length expressed in degrees of the mercury column above the cork.

*Specific Gravity.*—The specific gravity can be determined accurately enough by means of a Westphal balance making the determinations at room temperature and correcting to  $15^{\circ}\text{C}.$ , by using the factor .00083 for every degree centigrade difference from this standard temperature. The correction for temperature is large enough so that especial care must be taken to make the temperature readings accurately. In order to make specific gravity determinations with the Westphal balance on as small a fraction as is often desirable, it is necessary to have a smaller cell than that usually furnished with the instrument. This can readily be made by properly shortening a test tube with a diameter only slightly greater than the bob of the balance and supporting it in a flat cork. In this way the gravity of a fraction of only 18 grams (3.6 per cent) can readily be determined on a balance with a bob having a displacement of  $5^{\text{cc}}$ .

*Index of Refraction.*—The index of refraction can be determined with sufficient accuracy by means of an Abbé refractometer taking the readings at room temperature and correcting by means of the factor .00047 for every degree difference from the standard temperature of  $15^{\circ}$  centigrade. It has been found that this factor .00047 is more nearly correct for the general run of turpentine than .00049 (as recommended in Circular No. 152) and that the use of different temperature correction factors for different values of the index of refraction is not necessary in order to obtain the degree of accuracy required for the work.

<sup>1</sup> Young's "Fractional Distillation;" p. 12.

### *Recording Data*

A typical data sheet showing the original and corrected values as first recorded is shown in Table I. For the purpose of making the interpretation of these results simpler and easier the final corrected values for the boiling point, specific gravity, and index of refraction of the different fractions are plotted against the total percentage weight of these fractions. The curves resulting from plotting the data given in Table I are shown in Figure 2.<sup>1</sup>

### *Interpretation of Distillation Curves*

In order to properly interpret these curves it is necessary to understand the behavior of a mixture of liquids on distillation, and a brief discussion of fractionation by distillation and of distillation curves will therefore be given followed by a discussion of the curves obtained by the distillation of two different turpentines.

### *Discussion of Theoretical Boiling Point Curves*

Let us assume a mixture of equal quantities of two volatile liquids A and B with boiling points 160° C. and 200° C., respectively. If on distilling this mixture a complete separation of the two components was obtained then the distillation curves formed by plotting the percentage of distillate against the boiling point would be represented by the vertical lines AX and BY (Figure 3); that is, all of substance A in pure condition would distill over first and then the pure substance B.

*Fractionation by Ordinary Distillation.*—Such a complete separation is, however, never obtained because the boiling point of one liquid is always affected by the presence of another volatile liquid. In this case, some of the higher boiling substance B would distill over with A long before the temperature of the distillation reaches 200°, the boiling point of B, and some of the lower boiling substance A would be left in the flask even after the temperature had risen above 160° C. When a mixture like the above is

<sup>1</sup> In all the figures showing distillation curves, unless otherwise indicated in the figure itself, the full circles represent boiling points, the open circles, specific gravities and the half-open circles, indices of refraction.

TABLE I.—TYPICAL DATA SHEET SHOWING RECORDS OF DISTILLATIONS

| Fract.<br>No. | Temperature |    |     |     | Weight                           |       |                 | Percentage Weight        |                                | Specific Gravity |                         |                               | Index of Refraction |                         |                             |
|---------------|-------------|----|-----|-----|----------------------------------|-------|-----------------|--------------------------|--------------------------------|------------------|-------------------------|-------------------------------|---------------------|-------------------------|-----------------------------|
|               | T           | t  | T-t | n   | Flask<br>plus<br>Distil-<br>late | Flask | Distil-<br>late | Single<br>Frac-<br>tions | Total<br>Combined<br>Fractions | Deter-<br>mined  | Tempera-<br>ture<br>°C. | Calcu-<br>lated for<br>15 °C. | Deter-<br>mined     | Tempera-<br>ture<br>°C. | Calculated<br>for<br>15 °C. |
| 1             | 156.5       | 49 | 108 | .56 | 79.6                             | 32.1  | 47.5            | 9.5                      | 9.5                            | .8596            | 21.5                    | .8650                         | 1.4693              | 19.5                    | 1.4714                      |
| 2             | 157.0       | 50 | 107 | .57 | 94.1                             | 39.0  | 55.1            | 11.0                     | 20.5                           | .8597            | 21.5                    | .8651                         | 1.4694              | 19.5                    | 1.4715                      |
| 3             | 157.3       | 50 | 107 | .57 | 80.3                             | 25.3  | 55.0            | 11.0                     | 31.5                           | .8599            | 21.5                    | .8653                         | 1.4695              | 19.5                    | 1.4716                      |
| 4             | 157.7       | 51 | 107 | .57 | 97.6                             | 36.6  | 61.0            | 12.2                     | 43.7                           | .8601            | 21.5                    | .8655                         | 1.4699              | 19.5                    | 1.4720                      |
| 5             | 158.0       | 50 | 108 | .58 | 83.1                             | 28.3  | 54.8            | 11.0                     | 54.7                           | .8605            | 21.2                    | .8656                         | 1.4702              | 19.5                    | 1.4723                      |
| 6             | 158.8       | 50 | 109 | .58 | 96.7                             | 32.5  | 64.2            | 12.8                     | 67.5                           | .8609            | 21.2                    | .8660                         | 1.4707              | 19.2                    | 1.4727                      |
| 7             | 159.7       | 51 | 109 | .59 | 161.7                            | 77.4  | 84.3            | 27.3                     | 77.5                           | .8615            | 21.0                    | .8665                         | 1.4714              | 19.2                    | 1.4734                      |
| 8             | 162.4       | 51 | 111 | .62 | 96.2                             | 43.5  | 52.7            | 10.5                     | 88.0                           | .8625            | 21.0                    | .8675                         | 1.4730              | 19.2                    | 1.4750                      |
| 9             | 167.3       | 52 | 115 | .67 | 61.0                             | 27.1  | 33.9            | 6.8                      | 94.8                           | .8639            | 21.0                    | .8689                         | 1.4760              | 19.2                    | 1.4780                      |
| Resi-<br>due  |             |    |     |     | 150.6                            | 125.5 | 25.1            | 5.0                      | 99.8                           | .9408            | 20.0                    | .9450                         | 1.4914              | 21.1                    | 1.4913                      |



distilled from an ordinary distilling flask the distillation curve would therefore be more like curve I in figure 3. This curve shows that the composition of the distillate gradually changes throughout the distillation from pure A to pure B, the first 25 per cent of the distillate being nearly pure A and the last 25 per cent being nearly pure B.

*Fractionation by Dephlegmation.*—In order to obtain better separations of A from B in a single distillation some kind of a still head or dephlegmator is used, (such as the Hempel column shown in Figure 1) in which the ascending vapors are partially condensed and flow downward in liquid form to the distilling flask. The descending liquid comes in contact with more ascending vapors and there is an interchange of constituents, some of the low boiling material in the liquid being vaporized and some of the high boiling material in the vapors being condensed, with the result that the vapors which finally leave the top of the dephlegmator contain a larger proportion of the lower boiling material than the vapors which enter the dephlegmator from the flask. That is, there is a more complete separation of the components when the dephlegmator is used. Under such conditions the distillation curve would be more like curve II in figure 3, which indicates about 45 per cent practically pure A, about 10 per cent of a rapidly varying mixture, and the rest practically pure B.

*Summary.*—This consideration of the boiling point curve of a mixture of two components may be summed up as follows:

- (1) The more complete the separation the more accurately do the curves represent the composition of the mixture.
- (2) The more vertical curves indicate a more uniform substance in the distillate.
- (3) Curves more nearly horizontal indicate a distillate rapidly changing in composition.

#### *Distillation Curves of a Gum Turpentine*

The distillation curves for a turpentine are interpreted in a way similar to the theoretical curve in figure 3, but complications arise on account of the complexity of the mixture distilled and the incompleteness of the separation of some of the constituents.

Specific gravity and index of refraction are plotted, like the boiling point against percentage weight, and the three curves are considered together in interpreting the results of the distillation.

The curves in Figure 2 which give the results of the distillation of a gum turpentine, might be interpreted in the light of the previous discussion, as indicating a composition of about 95 per cent of some substance, "a," with boiling point  $158^{\circ}$  C., specific gravity .865, and index of refraction 1.4714 and about 5 per cent of some other material, "b," with values of all properties considerably higher (say specific gravity .95, index 1.489); the gradual increase in the values of all the physical properties from the first fraction up to 95 per cent might be thought to be due to a gradually increasing proportion of this high boiling and heavy material in the distillate (as was the case in the boiling point curves of Figure 3). But this interpretation is shown to be incorrect by the procedure described below which was carried through for an entirely different purpose (See page 62).

Figure 13 gives the result of a distillation of a part of the turpentine used in Figure 2, which had been redistilled several times in order to remove the high boiling and heavy material originally present. The curves show that this heavy material "b" has been entirely removed and yet the values for all the physical properties increased to some extent as the distillation progressed indicating that the distillate was not a pure substance. Evidently then the gradual increase of these values in Figure 2 was not (or at least not entirely) due to the presence of "b" in the first 95 per cent of the distillate, but instead there must be present another substance "c" with physical properties only slightly higher than those of "a," the boiling points of "a" and "c" being so close together that the substances are very incompletely separated by distillation.

This interpretation agrees with the results of recent investigations on the chemical constituents usually present in turpentine. According to Semmler<sup>1</sup> there may be present in American turpentine besides pinene<sup>2</sup> two other terpenes, camphene and

<sup>1</sup> "Die Aetherische Oele" Vol. II, pages 55 and 274.

<sup>2</sup> Boiling point,  $155^{\circ}$ – $156^{\circ}$  C., specific gravity .863; index of refraction 1.4678.

nopinene.<sup>1</sup> The physical properties of these two terpenes have not been accurately determined, but it is sufficient to know that they are all higher than those of pinene. The first 95 per cent of the distillate from this turpentine was probably composed of a mixture of pinene with either camphene and nopinene, or both, and the last 5 per cent was made up of materials with much higher physical properties, probably oxidation products of the terpenes.

In the distillation of turpentine by this method the separation between the terpenes and the high-boiling non-terpenes is sufficiently complete so that the physical properties of the first fractions are not appreciably influenced by the presence of materials with boiling points 30°—35° higher. The mixture of the terpenes—pinene, camphene and nopinene is, however, not sufficiently well separated to make it possible to estimate the proportions of the different constituents, and it will hereafter in this paper be designated as “pinene” unless for any reason it is necessary to mention the other constituents.

#### *Distillation Curves of a Wood Turpentine*

The curves obtained by the distillation of a wood turpentine (Figure 54) show this to be sufficiently different in composition from the gum turpentine just discussed that new points in the interpretation of the curves are introduced. The first 70–75 per cent of the distillate could well be, from the physical properties, a mixture of the same terpenes which are the main constituents of the turpentine shown in Figure 2, the slightly lower physical properties being accounted for by smaller proportions of either nopinene or camphene, or both. But between the points where 70 and 95 per cent distill the specific gravity of the distillate decreases while the boiling point and index of refraction increase. This indicates the presence of some substance with higher boiling point and higher index of refraction, but with lower gravity than “pinene.” There is a terpene—dipentene—whose physical properties correspond well with those required by this substance; it has a higher boiling point (175°C.), a lower specific gravity (.849 at 15° C.), and higher index of refraction (1.471 at 15° C.)

<sup>1</sup> The physical properties of both about the same at the following values: Boiling point, 160°–165°; specific gravity, .874; index of refraction, 1.4724.

than "pinene;" it is known to be one of the products of the action of high temperatures on pinene;<sup>1</sup> it has been identified as one of the constituents of wood turpentine produced in Finland and Russia;<sup>2</sup> and its presence in American "pine tar oil" has been indicated.<sup>3</sup> It is quite probable therefore that the substance whose presence is indicated by the marked decrease in specific gravity of the fractions as the boiling point approaches 175° C. is dipentene, and that it is formed from "pinene" by the high temperature employed in removing the turpentine from the wood.

*Chemical Identification of Dipentene.*—In order to make sure that dipentene was present in this turpentine, however, an identification by chemical means was carried out. By repeated fractional distillation, and final distillation over sodium, a considerable quantity of material was obtained with boiling points 172°–174.1° C., specific gravity .8527 at 15° C. and index of refraction 1.4771 at 15° C. Part of this material was treated with bromine in glacial acetic acid<sup>4</sup> and crystals were obtained which, after six crystallizations from ethyl acetate, melted at 125°–125.5° C., (dipentene tetrabromide 125°–126° C.) thus substantiating the conclusions regarding the presence of dipentene which were originally drawn from the physical properties. It seems very likely therefore that when a turpentine obtained from the long-leaf pine is distilled by the method described above, a decrease in specific gravity as the boiling temperature approaches 175° C. is a good indication of the presence of dipentene.

*Completeness of Separation of Constituents.*—The exact percentage of dipentene can not be determined from the curves in figure 54, since the separation between the "pinene" and the dipentene is not sufficiently sharp; there are small quantities of dipentene in the portion distilling between 70 per cent and 80 per cent as shown by the slight decrease in specific gravity, but it is only in the portion coming over after 80 per cent has been distilled that there are comparatively large quantities of dipentene

<sup>1</sup> Wallach, Ann. Chem. 227, 282.

<sup>2</sup> Aschan and Hjelt. Chem. Ztg. 18, 1566.

<sup>3</sup> Kremers, Pharm. Rev. 22, 150.

<sup>4</sup> Heusler-Pond, "Chemistry of the Terpenes," Pp. 73 and 95.



present (as shown by the decided changes in direction in the boiling point and index of refraction curves). The separation between the dipentene and the "heavy oils" is, however, quite complete, and the percentage of the latter can be determined with considerable accuracy. This turpentine contains then 95 per cent of terpenes (containing approximately 80 per cent "pinene" and 15 per cent dipentene) and 5 per cent of heavy, high boiling oils, probably non-terpenes.

Other points in the interpretation of distillation curves will be discussed as required in connection with the numerous analyses recorded on the following pages.

#### *Comparison of Fractionations Obtained by Different Methods of Distillation*

In order to show the advantages gained by the use of a dephlegmator, and by the use of direct distillation instead of steam distillation, the following distillations were carried out on the same turpentine: (1) Steam distillation without a dephlegmator, (2) direct distillation without a dephlegmator, (3) steam distillation with a Geer dephlegmator as described in Forest Service Circular No. 152, and (4) direct distillation through a five bulb Le Bel-Henninger dephlegmator. The last named will not be described because another form of dephlegmator was afterward adopted as most suitable for general work.

#### *Steam Distillation with and without a Dephlegmator*

In Figure 4 are plotted together on one sheet for better comparison the curves obtained by steam distillation both with and without a dephlegmator.<sup>1</sup> The curves showing the results obtained by the use of a dephlegmator indicate the better fractionation since they are more nearly vertical and have lower values over the first part of the distillation, and the breaks in the

<sup>1</sup> In the case of these distillations, and of all the rest of the analyses mentioned in this article, the original and corrected data will not be given, but only the curves obtained by plotting the corrected data; the curves are all that it is necessary to have in order to obtain the complete interpretation of the results, and there are so many distillations recorded in the following pages that the space required by the tabulated data would be prohibitive.

general direction are more marked than in the curves which give the results obtained by steam distillation without a dephlegmator.

*Direct Distillation with and without a Dephlegmator*

A still greater effect obtained by the use of a dephlegmator is indicated in Figure 5 where are plotted together the curves from two direct distillations, one with and one without a dephlegmator. Here the differences in the position and direction of the curves and therefore in the fractionation, are even more marked than in Figure 4.

*Steam and Direct Distillation with Dephlegmators*

Figure 6 gives a comparison of the fractionation obtained by steam distillation through a Geer dephlegmator with that by direct distillation through a Le Bel-Henninger dephlegmator. In the direct distillation curves there are all the evidences of better fractionation, i.e., lower values for the physical constants of the fractions over the first part of the distillation, more nearly vertical curves, and sharper breaks in the direction of the curves. On account of the better fractionation it is possible to judge the composition of the turpentine with a considerable degree of accuracy and it apparently contains very nearly 80 per cent of "pinene" the remainder being heavy oils with all the physical properties much higher. From the steam distillation curves, on the other hand, it would be impossible to make an accurate judgment of the proportion of "pinene" present in the turpentine, because the separations are so incomplete and the curves change direction so gradually. The distillate is practically pure "pinene" up to about 70 per cent, but for some distance beyond that point it is an indefinite mixture of "pinene" with heavier and higher boiling materials.

*Steam and Direct Distillation with Dephlegmators and Direct Distillation without a Dephlegmator*

Similar distillations were made on another kind of turpentine (refined turpentine No. 5) giving even more striking differences in the separations obtained. Figure 7 shows the results obtained by fractionating three samples of the same turpentine (1) by

steam distillation with a Geer dephlegmator (2) by direct distillation without a dephlegmator and (3) by direct distillation with a Le Bel-Henninger dephlegmator, the three sets of curves being plotted together on one sheet for easier comparison. The curves obtained by steam distillation with a dephlegmator, and by direct distillation without a dephlegmator show very similar characteristics; there are no rapid changes in direction until about 90 per cent is reached and then there is a rapid increase in all the physical constants; that is, these curves indicate about 90 per cent "pinene" and about 10 per cent of material with all physical constants higher. The curves obtained by direct distillation with a dephlegmator are, however, quite different; they indicate that there are three main constituents of this turpentine sufficiently different in boiling points and other properties so that approximate determinations can be made of the proportion of each, these proportions being about 80 per cent of "pinene," 15 per cent of dipentene, and 5 per cent of heavy residue. In the distillation by the first two methods the dipentene was not sufficiently well separated from the other constituents so that its presence was sharply indicated, the very slight and very gradual decrease in the specific gravity over the first 80 per cent of the distillation being the only sign of the presence of such a substance.

#### *Steam and Direct Distillation with Dephlegmators*

Another comparison of the results obtained by steam and direct distillation, both through a dephlegmator, is given in Figure 8, in this case on a still more complex turpentine. The curves obtained by the direct distillation with a Le Bel-Henninger dephlegmator indicate that this turpentine is composed of about 11 per cent "light oils" (with boiling points below those of "pinene"), about 32 per cent of "pinene," about 22 per cent of dipentene and 35 per cent of heavy oils. The separation between the "pinene" and the dipentene was not very sharply indicated (that is, the breaks in the direction of the curves are not very marked) but the amount of light oils, of turpentine oils ("pinene" and dipentene) and of heavy oils are quite accurately determined. In the steam distillation curves, however, no sharp separations of

the turpentine into its constituents are shown (that is, there are no sharp breaks in the curves). The presence of dipentene is not even indicated qualitatively, and the proportion of heavy oils (as in figure 6) can not be judged within 8 to 12 per cent.

### *Conclusions*

These examples of the results obtained in the fractionation of three different turpentines by different methods of distillation have shown very clearly that, so far as the completeness of the separations and the corresponding ease and accuracy of the interpretation of the results are concerned, direct distillation through a dephlegmator is the best distillation method for the analysis of turpentines.

### *Alterations in Composition during Distillation*

A possible objection to such a method is mentioned in Forest Service Circular 152<sup>1</sup>; viz., that the higher temperatures required would be likely to decompose some of the oil during the distillation so that the fractions would not represent the true composition of the original material. In those distillations described above in which the same turpentine was distilled by the two methods, there were no evidences of decomposition in any case except that the residues left in the distilling flask were usually darker in color when direct distillation had been used; the differences in the curves obtained by the two methods were of such a nature as would indicate only different fractionation.

### *Changes in Physical Properties due to Boiling at Different Constant Temperatures*

*Crude Wood Turpentine.*—In order to obtain some idea of the comparative effects of different methods of distillation on the physical properties of turpentines, two samples of the same turpentine (turpentine No. 4) were boiled under conditions similar to those of steam and direct distillation (that is, with and

<sup>1</sup> "The Analysis of Turpentine by Fractional Distillation with Steam," by William C. Geer.



without water being present) and the specific gravity and index of refraction were determined at regular intervals; in both cases a well cooled reflux condenser was used so that the loss was negligible. The effects of boiling under these two sets of conditions are shown graphically in Figure 9. By boiling in the presence of water at a temperature of about  $94^{\circ}$  C., the gravity of the turpentine was increased very slightly the first hour and after that decreased very slightly every hour until the boiling was stopped. By the boiling without the presence of water at a temperature of about  $162^{\circ}$  C., the gravity increased at the rate of .00045 per hour for the first two hours, and then at a much slower rate. The index of refraction was increased considerably by both methods of boiling during the first two hours and then more slowly.

*Refined Wood Turpentine.*—The results from a similar series of experiments on another turpentine (turpentine No. 5, the analysis of which is shown in Figure 7) are expressed graphically in Figure 10. Here the changes in the physical properties due to either method of boiling are less than were shown in Figure 9, being within the limit of the possible experimental error in some cases. But the same general tendency of the specific gravity to be slightly increased by the direct boiling and slightly decreased by the boiling with water is shown as in Figure 9. The index of refraction is, however, slightly decreased by the boiling with water instead of being increased, as in the previous case.

*Conclusions.*—The effect of the boiling on the physical properties of the turpentines is apparently not very great in either case, but for two reasons the results obtained are not conclusive: (1) The temperature to which the turpentines were subjected were only as high as would prevail at the very beginning of distillation, and therefore in the case of the direct distillation, probably do not come within  $40^{\circ}$  C. of the temperatures reached at the end of a regular fractional distillation; (2) Different components of the turpentine might have the physical properties changed in different directions and thus the changes in the properties of the turpentine as a whole would not show the actual changes in composition which had taken place.

*Changes in Physical Properties under Conditions of Fractional Distillation*

Another method for comparing the changes in composition due to steam distillation and direct distillation was carried out as described below.

*Direct Distillation of Crude Turpentine.*—Crude turpentine No. 4 was repeatedly redistilled by direct distillation through a Le Bel-Henninger dephlegmator, each time rejecting the heavy residue left in the flask and as much of the distillate as showed especially high physical properties; for instance, the first distillation was similar to the direct distillation shown in Figure 6, and the fractions up to 79.5 per cent formed the material for the next distillation, the residue and the last fraction of the distillate being rejected. The curves showing the course of the third and fourth distillations were practically identical and are both represented by the curves in Figure 11. All the heavy oils present in the original turpentine must have been removed by the first two distillations, otherwise the physical properties of the residue would have been higher in the third distillation than in the fourth. Since the original heavy oils had been completely removed, the higher physical properties of the residue in the third and fourth distillations must be due to the heavy oils formed during the course of the distillations. The difference in the values of the physical constants between the last fraction and the residue in Figure 11 is therefore an approximate measure of the change in composition due to the temperature of the distillation. The lack of any marked difference in properties between the first and second fractions indicates that there was no appreciable decomposition into substances with lower boiling points.

*Steam Distillation of Crude Turpentine.*—In order to obtain, for comparison, the change in composition due to distillation with steam, all the material represented by Figure 2, except the residue, was twice distilled by steam through a Geer dephlegmator. The curves for these two distillations were practically identical and are shown in Figure 12. Reasoning in the same way as above the difference in physical properties between the last fraction and the residue indicate the change in composition due to the dis-

tillation. This change is appreciable in the case of the steam distillation, but is somewhat less than in the direct distillation.

*Direct Distillation of Gum Turpentine.*—The same determination was made on a gum turpentine (the one whose analysis is shown in Figure 2). In this as in case of the wood turpentine the third and fourth distillations gave nearly identical curves which are shown in Figure 13. The amount of change in composition is also very nearly the same as in the case of the wood turpentine shown in Figure 11.

*Conclusions.*—It is evident then that under the conditions prevailing in the distillation shown in Figures 11 to 13, the amount of change in composition during analysis is very slight either in steam or direct distillation. This change apparently consists in the polymerization of a portion of the terpenes to substances with higher physical constants, and seems to take place mostly during the very last part of the distillation when the amount of oil in the distilling flask has become very small and when there is therefore a better chance for the sides of the flask to become superheated.

#### *Effect of Alterations on Interpretations of Curves*

*Turpentines Containing no Heavy Oils.*—When a turpentine containing no heavy oils is distilled by direct heat the undistilled residue left in the flask will contain a small amount of heavy oils owing to changes occurring during the distillation and the specific gravity and index of refraction of this residue will be higher than those of the last distilled fraction; the curves will therefore seemingly indicate that a small amount of heavy oils was present in the original turpentine, but from the curves of figures 11 and 13 the effect of the changes which occurred during the distillation can be determined, and the interpretation of the curves can be altered to correspond. For instance, in the distillation of 95 per cent of a turpentine containing no heavy oils, the production of heavy oils during the distillation will be sufficient to increase the gravity and index of the residue of 5 per cent by .0035 and .0040 respectively. Of course, if the residue is made smaller, say 2 per cent, then the apparent effect would be greater since there is a chance for more polymerization during the distillation

of that portion between 95 and 97 per cent, and the proportion of heavy oil to turpentine oil in the undistilled residue is increased (and hence the physical properties increased) as the distillation progresses. It is therefore necessary to leave about 5 per cent of oil undistilled in order to be able to correct accurately for the effect of polymerization.

*Turpentines Containing Heavy Oils.*—When, however, the turpentine to be distilled contains some heavy residue (as for instance in Figure 2) the conditions are somewhat different than in the above cases; the terpenes may all be distilled over and the residue left in the flask would then be all heavy oils; now these heavy oils might be changed by the heat more or less than the terpenes were in figures 11 to 13, but there is really no necessity for determining this change accurately because a small change in the physical properties does not affect the interpretation of the curves. For instance, if in Figure 2 the gravity of the residue had been .930 instead of .945, the composition of the turpentine as interpreted from the curves would still have been 95 per cent "pinene" and 5 per cent heavy residue; that is, a gravity of .93 is sufficiently higher than that of the terpenes so that the presence of a considerable amount of terpenes in the residue is excluded, and the only interpretation of the composition of the residue which it is possible to attempt is that it does not contain terpenes in considerable quantities.

*Conclusions.*—The change in composition of a turpentine during analysis by direct distillation is without effect on the interpretation of the results except in case there is no high boiling and heavy residue present in the original material, and in this case the approximate effect is known and the results can be corrected.

#### *Choice of a Dephlegmator*

The Le Bel-Henninger dephlegmator often mentioned in the foregoing has been used with good results in many turpentine analyses; it is efficient in fractionating power, and when properly constructed gives no trouble in filling up with liquid; the only objections to it are its cost and fragility. The simplest, least expensive and least fragile dephlegmator is of the Hempel column



type, and several different sizes of Hempel columns were tried to find if a practicable sized Hempel would give as good separations as the Le Bel-Henninger previously used. It was found that the Hempel column shown in Figure 1 gave slightly better separations than the five-bulb Le Bel-Henninger which has been used previously; a comparison between the results obtained by the use of these two dephlegmators is shown in Figure 14. The main difference between the curves obtained by the two types of dephlegmators is in the specific gravity in the vicinity of 90 per cent; the fractions obtained by distillation through the Hempel column have a lower gravity over this part of the curve, indicating a purer dipentene and therefore better fractionation; the sharper break in the curves at about 80 per cent also indicates better fractionation. On account of the simplicity and cheapness of the Hempel column as well as its better fractionation, it is recommended as the preferable dephlegmator for turpentine distillations. This type of dephlegmator has been used in making many of the distillations recorded in the following pages, and has given very satisfactory results.

## REFINING

The refining was done on five samples of crude wood turpentine collected from commercial plants using widely varying processes. A brief description of each of these processes will be given with the discussion of the work done on the samples. The apparatus used in the refining, and the method of conducting the distillations will be described first since the same arrangement of apparatus and the same general method was used in the refining of all the samples, and the description will therefore apply to all.

### *Description of Apparatus*

The refining still was of the continuous type with two phases, giving two distilled products and one undistilled residue. It was designed by the makers especially for this work since stills of this type for the refining of turpentine had not previously been used or manufactured in this country.

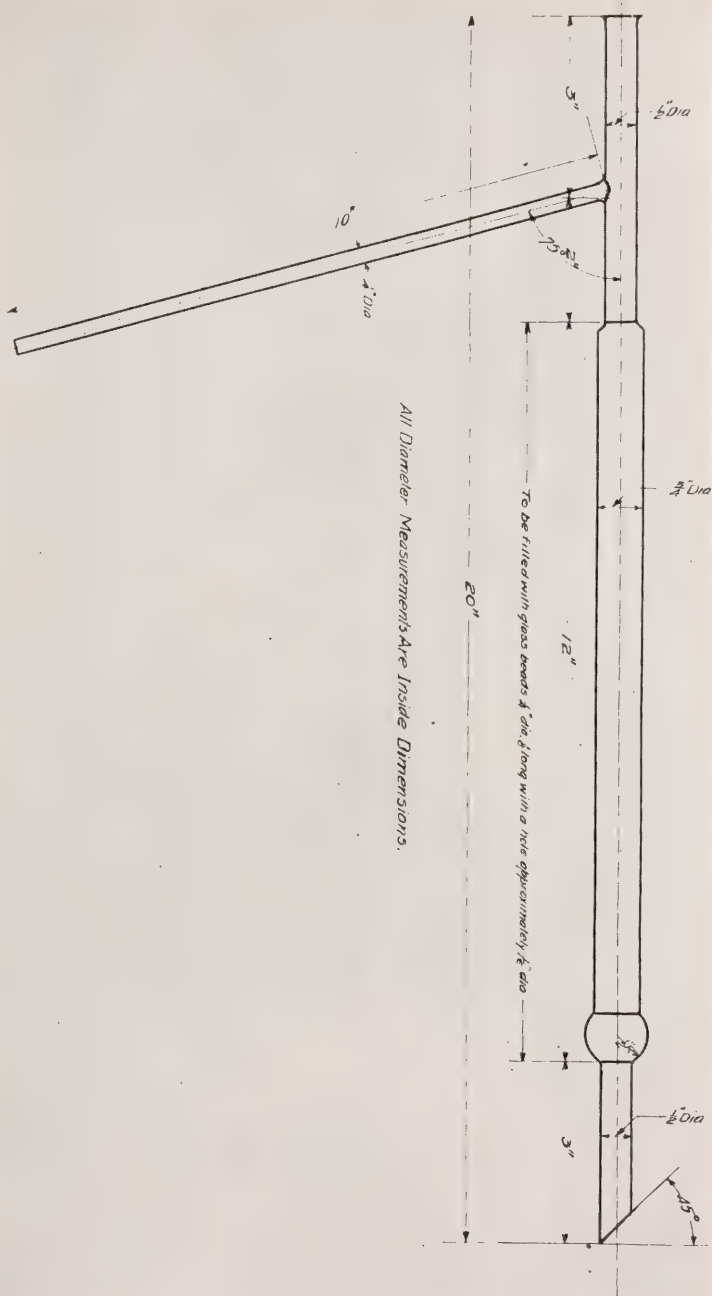


Fig. 1.  
Hempel Column.

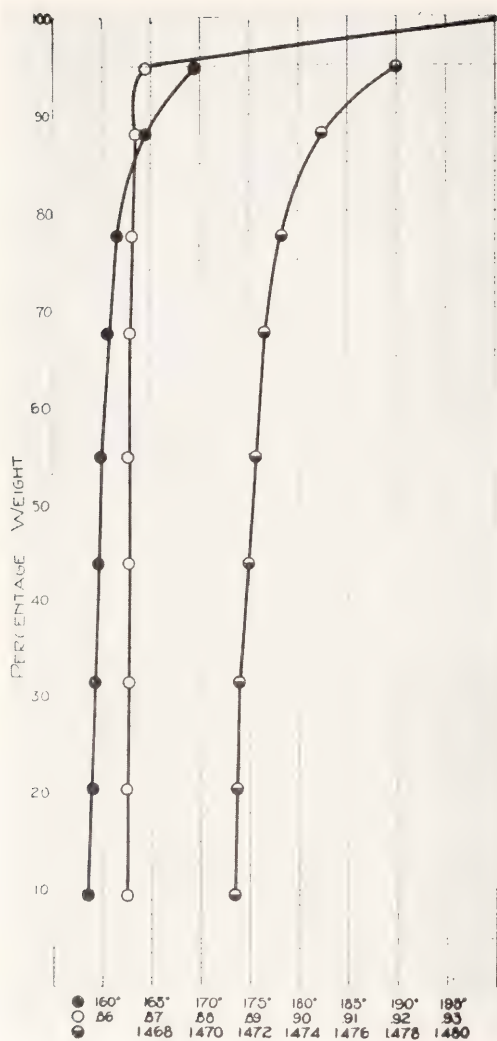


Fig. 2.

Typical curves showing boiling points, specific gravities, and indices of refraction of a gum turpentine.

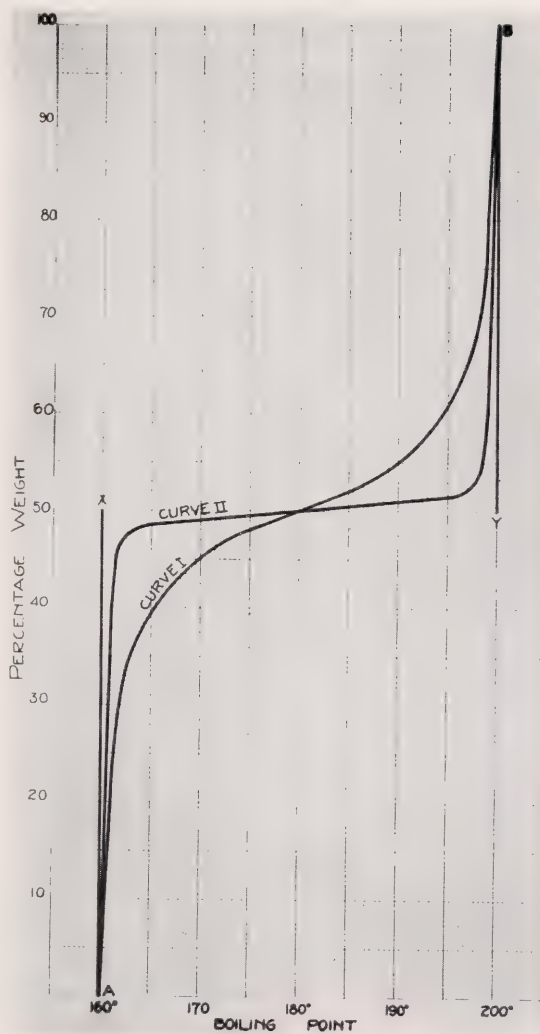


Fig. 3.  
Curves illustrating theory of fractional distillation.



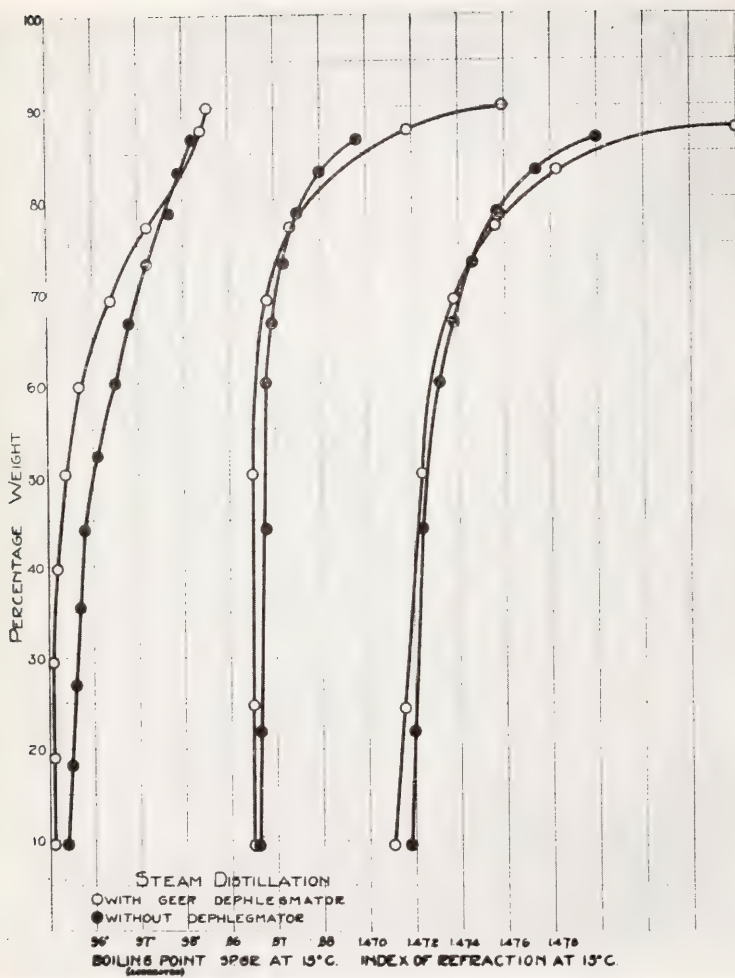


Fig. 4.

Comparison of fractionation obtained in steam distillation with a Geer dephlegmator and without a dephlegmator.

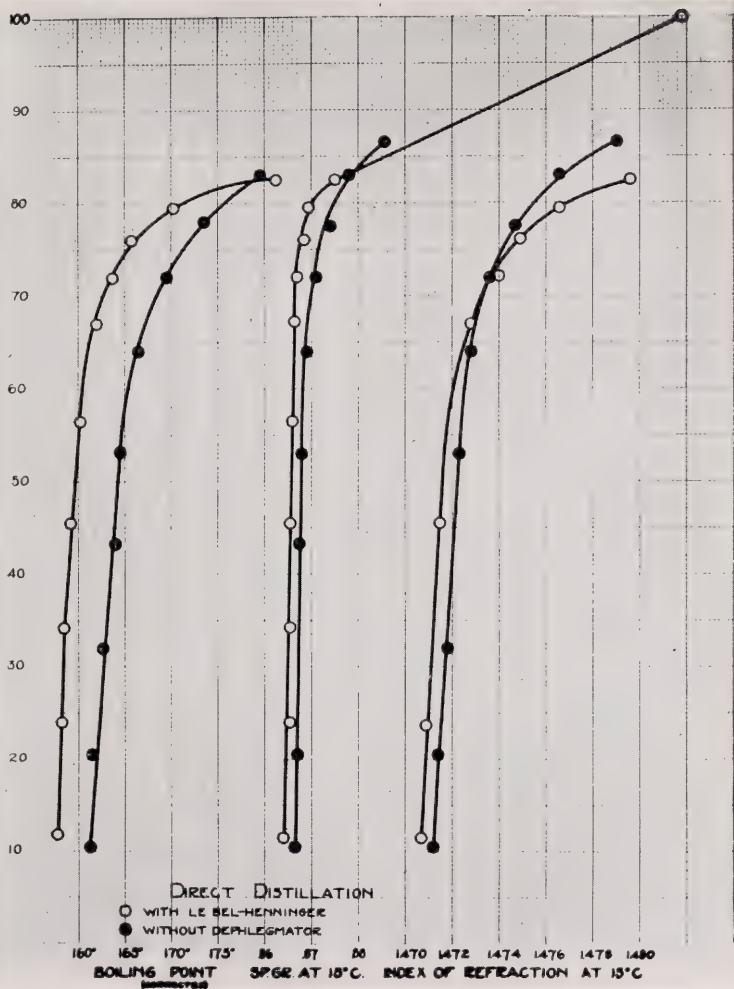


Fig. 5.

Comparison of fractionation obtained in direct distillation with a Le Bel-Henninger column and without a dephlegmator.



Fig. 6.

Comparison of fractionation obtained by steam distillation with a Geer dephlegmator and direct distillation with a Le Bel-Henninger dephlegmator.

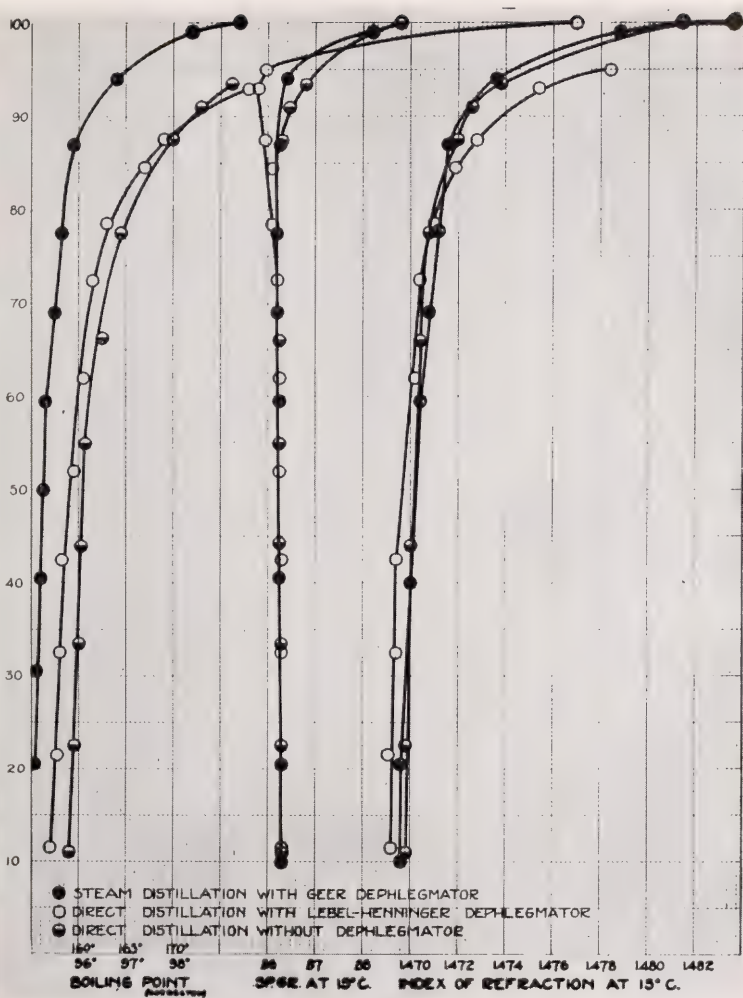


Fig. 7.

Comparison of fractionation obtained by (1) steam distillation with a Geer dephlegmator, (2) direct distillation with a Le Bel-Henninger dephlegmator, and (3) direct distillation without a dephlegmator.



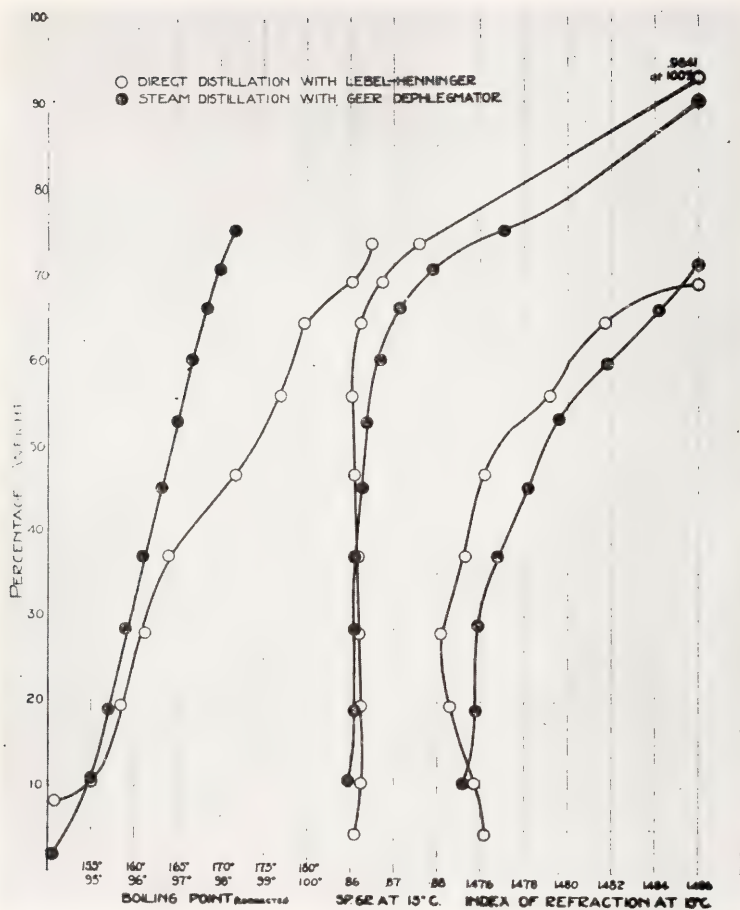


Fig. 8.

Comparison of fractionation obtained by direct distillation with a Le Bel-Henninger dephlegmator and steam distillation with a Geer dephlegmator.

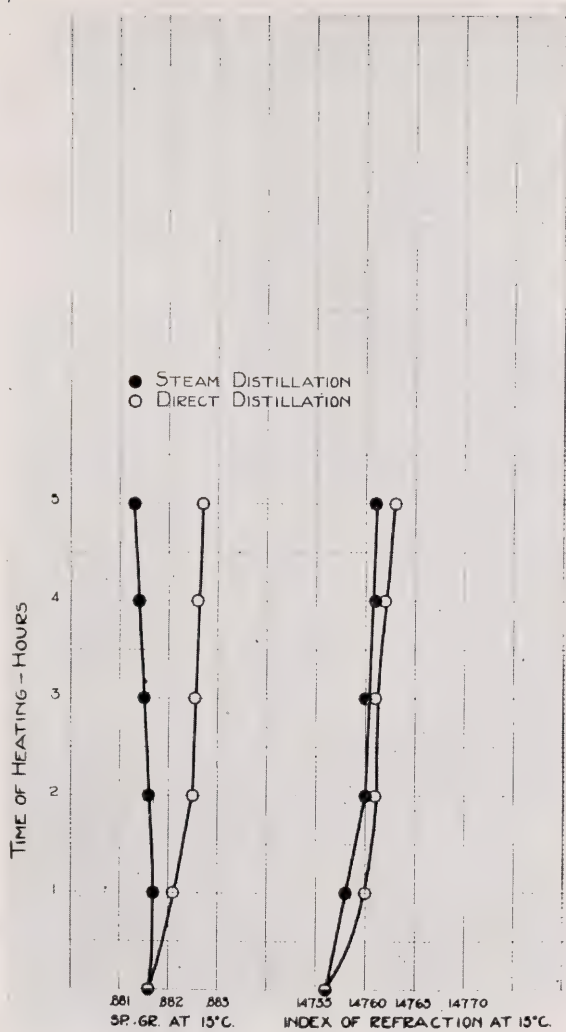


Fig. 9.

Effect of boiling in the presence of water (steam distillation) and of boiling without water (direct distillation) on the specific gravity and index of refraction of crude wood turpentine.

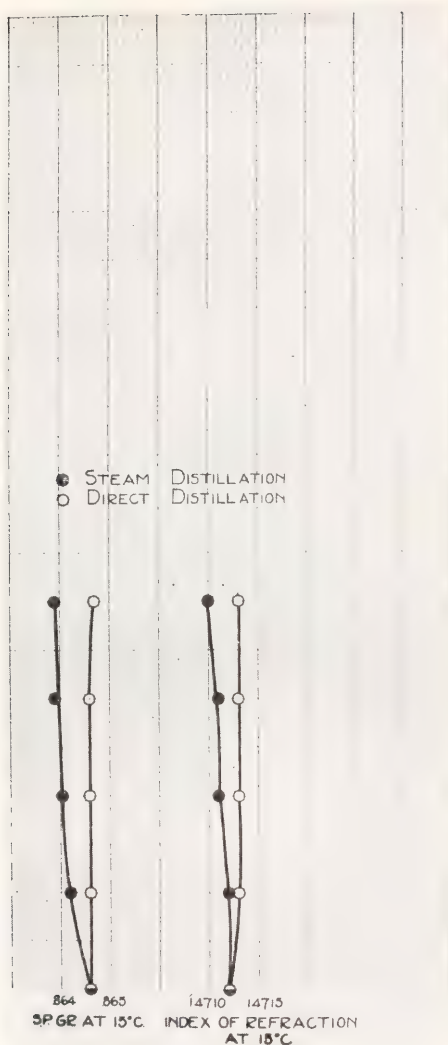


Fig. 10.

Effect of boiling in the presence of water (steam distillation) and of boiling without water (direct distillation) on the specific gravity and index of refraction of refined wood turpentine.

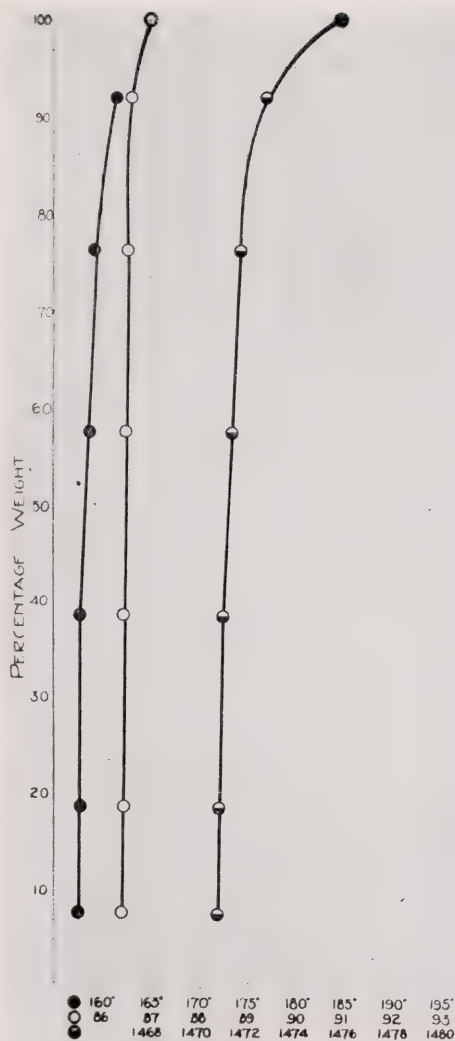


Fig. 11.

Alteration in physical properties of a crude wood turpentine due to direct distillation.



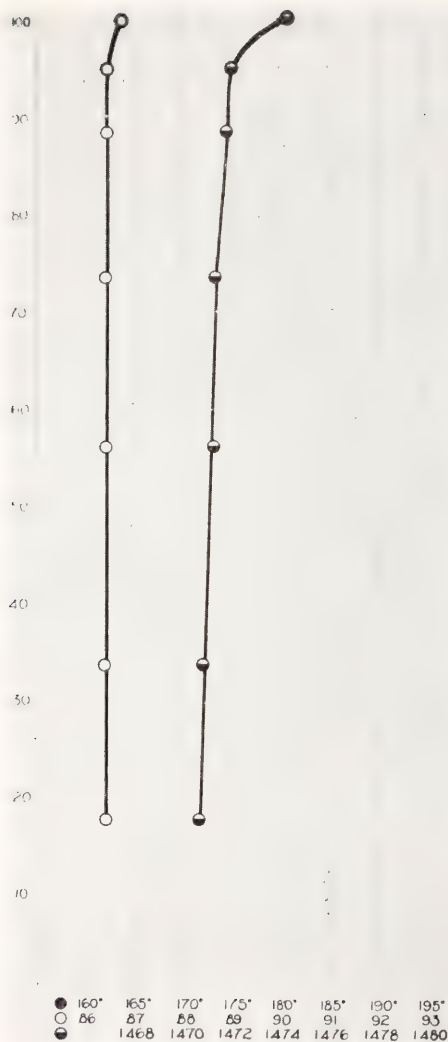


Fig. 12.

Alteration in physical properties of a crude wood turpentine due to steam distillation.

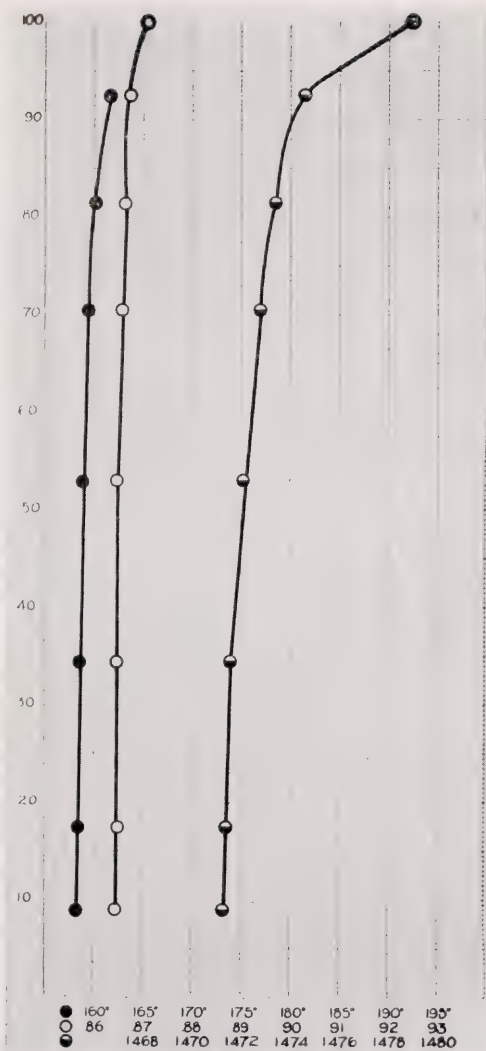


Fig. 13.

Alteration in physical properties of a gum turpentine due to direct distillation.

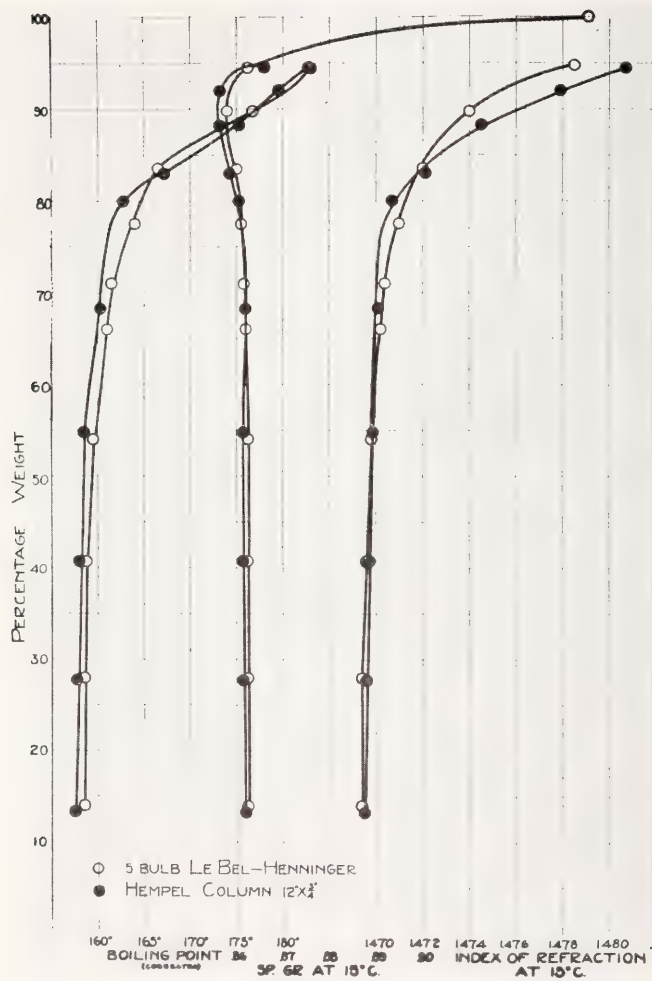


Fig. 14.

Comparison of fractionation with Le Bel-Henninger and Hempel column dephlegmators.

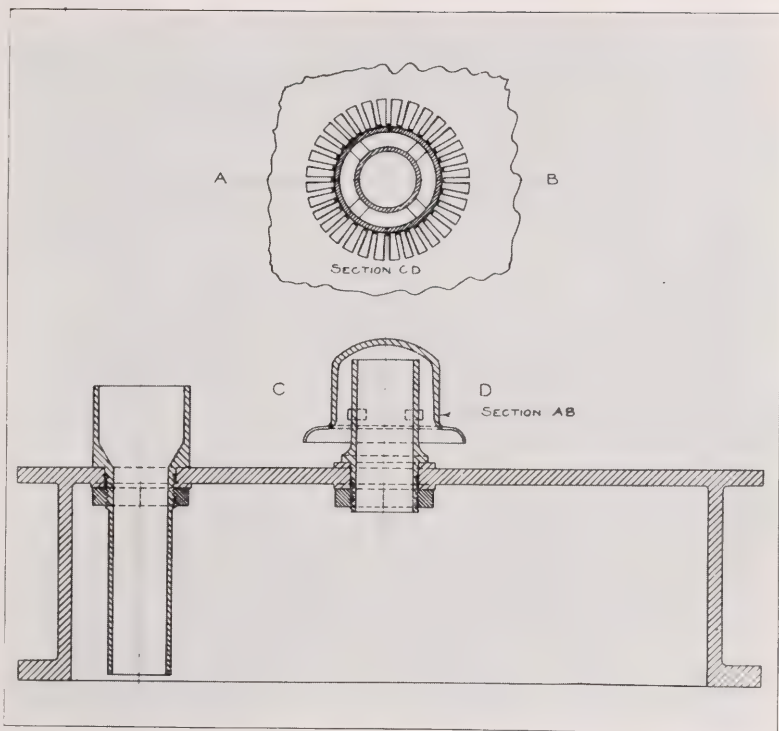


Fig. 15.  
Boiling cap sections.

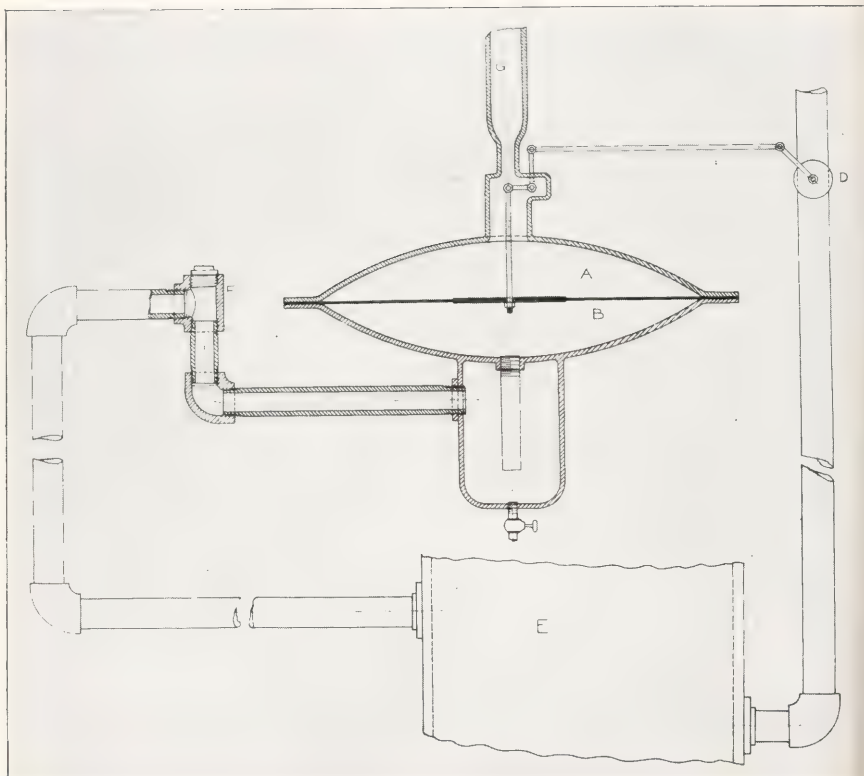


Fig. 16.  
Pressure regulator.



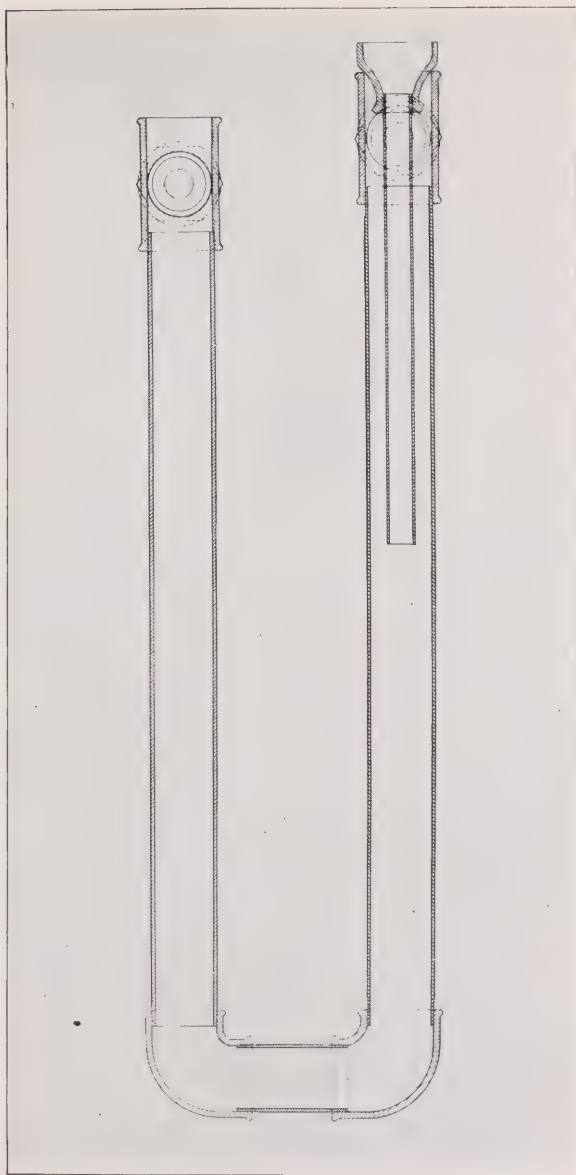


Fig. 17.  
Separator.

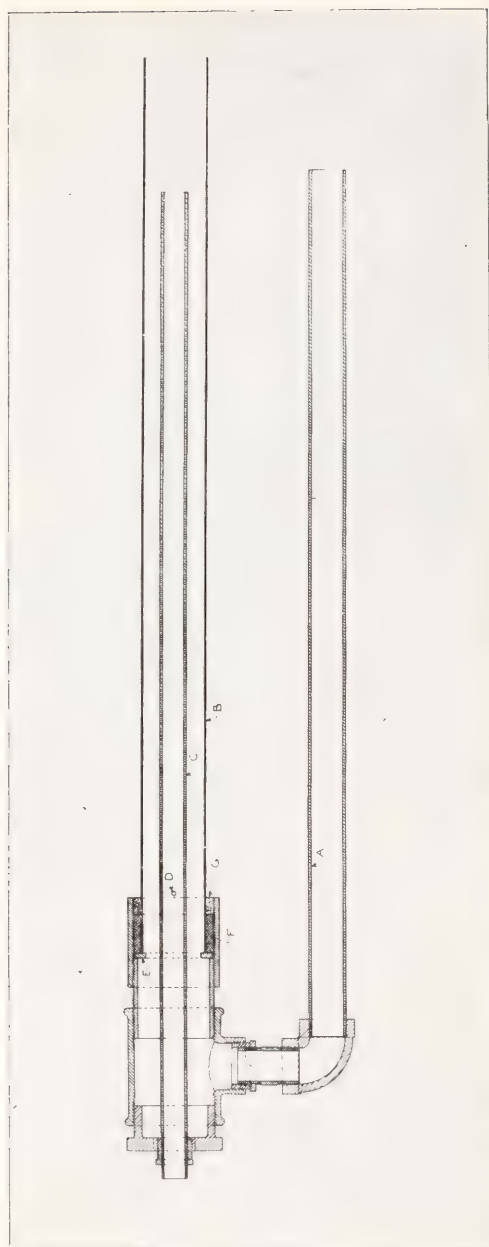


Fig. 18.  
Speed Indicator.

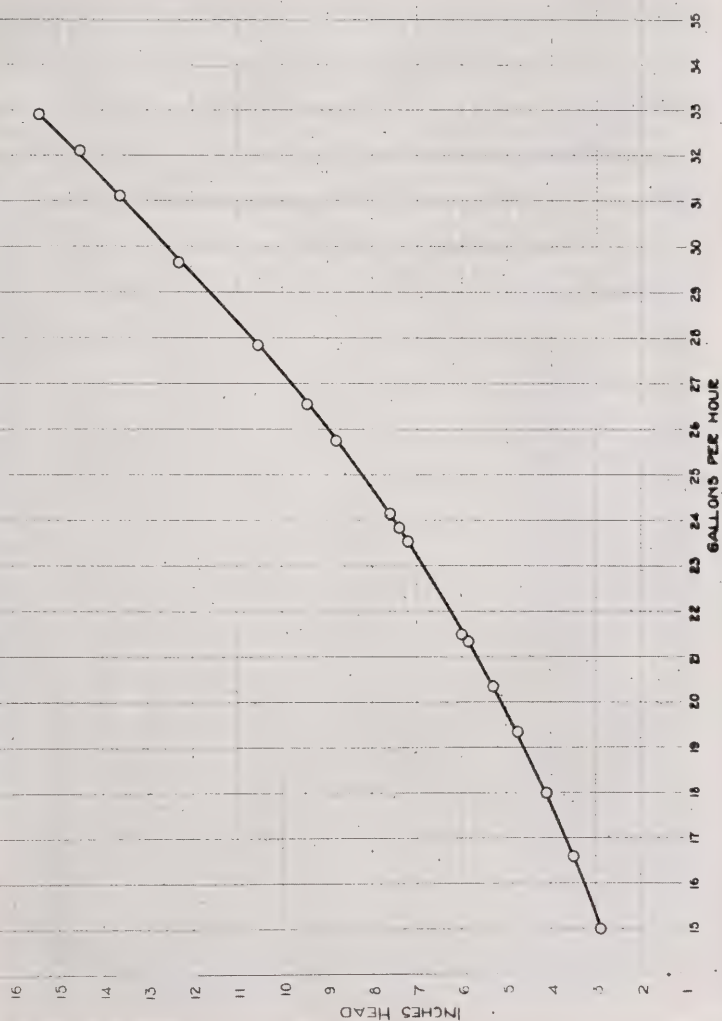


Fig. 19.  
Calibration curve for crude turpentine "speed indicator."

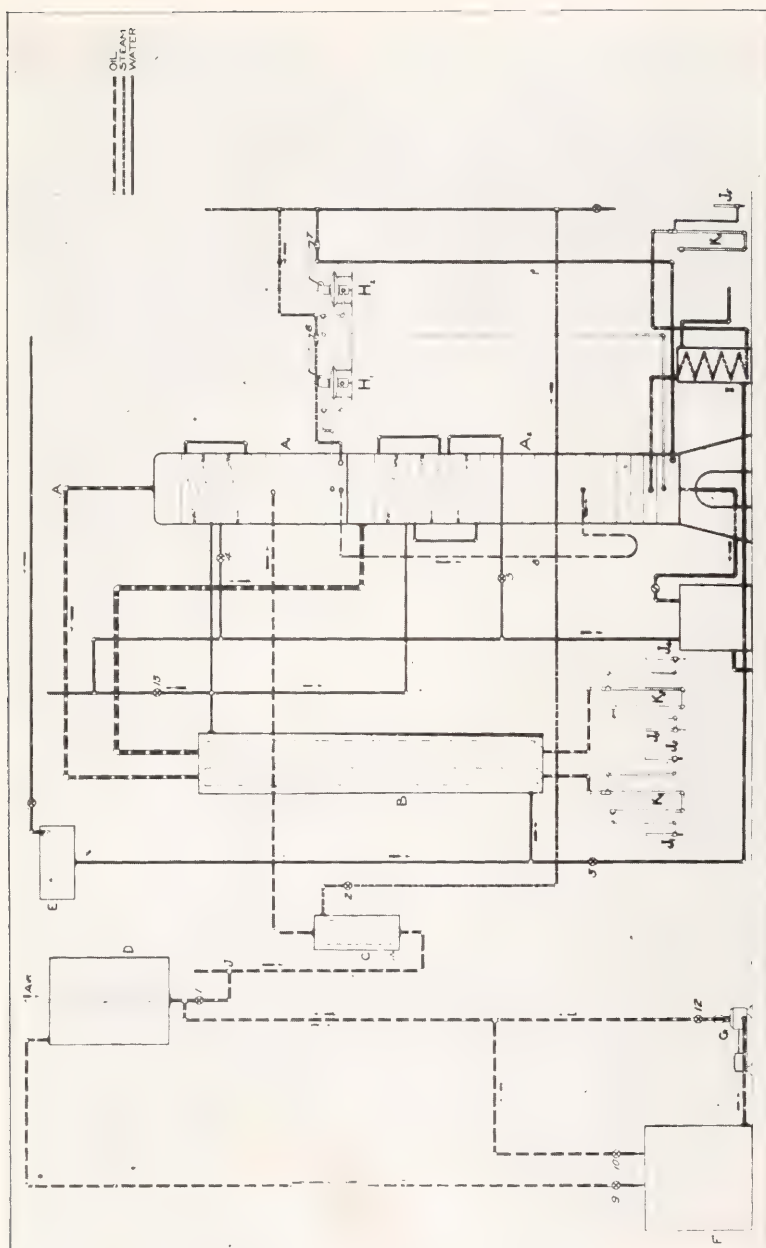


Fig. 20.  
General arrangement of apparatus for refining crude turpentine.

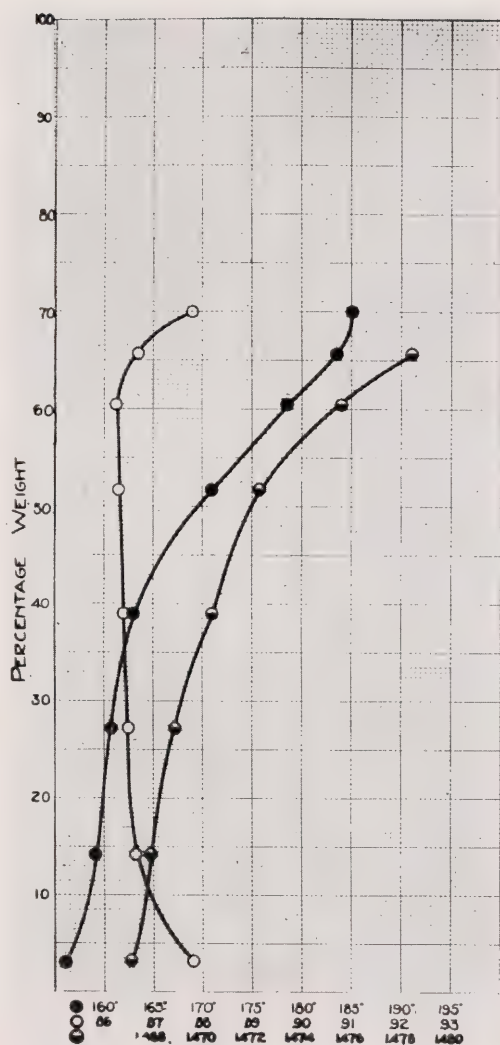


Fig. 21.

Boiling point, specific gravity and index of refraction curves for crude turpentine No. 1, untreated.



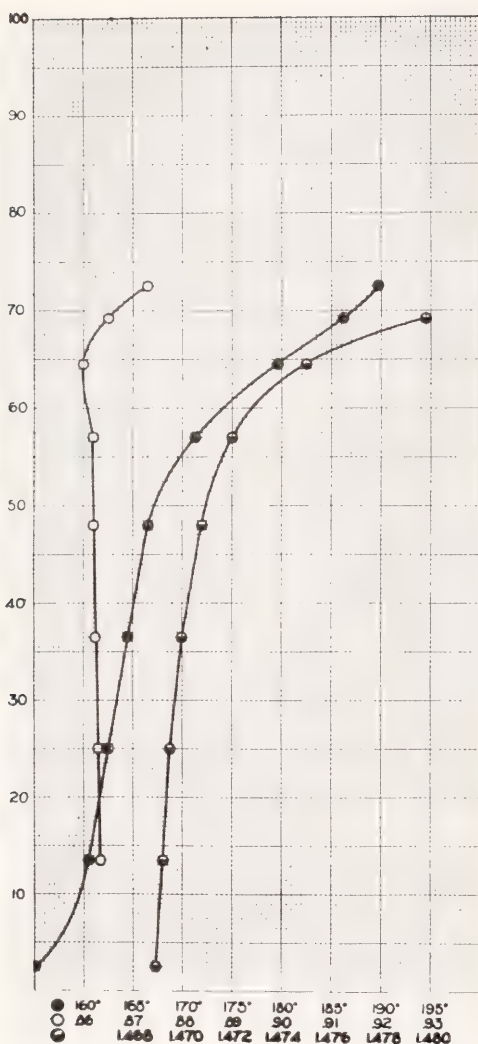


Fig. 22.

Boiling point, specific gravity and index of refraction curves for crude turpentine No. 2, after treatment with caustic soda solution.

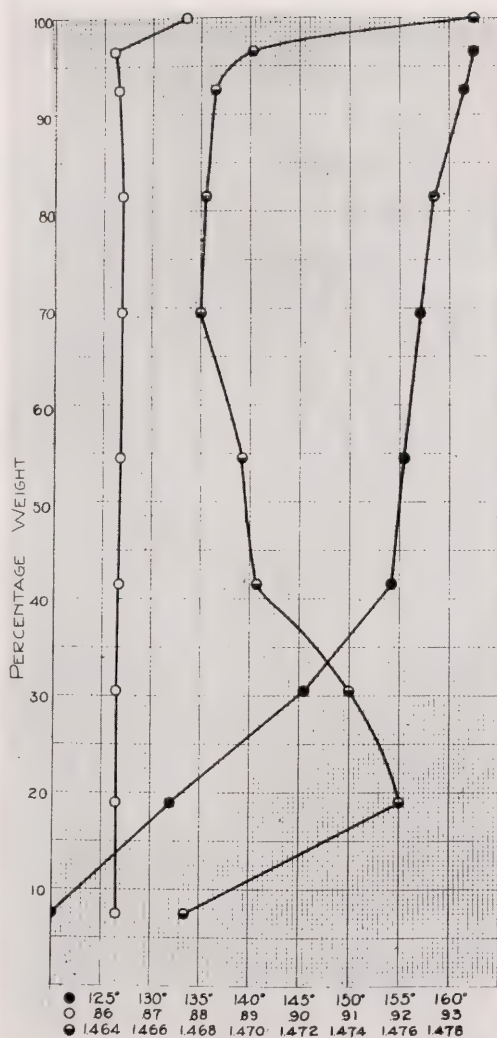


Fig. 23.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 1.

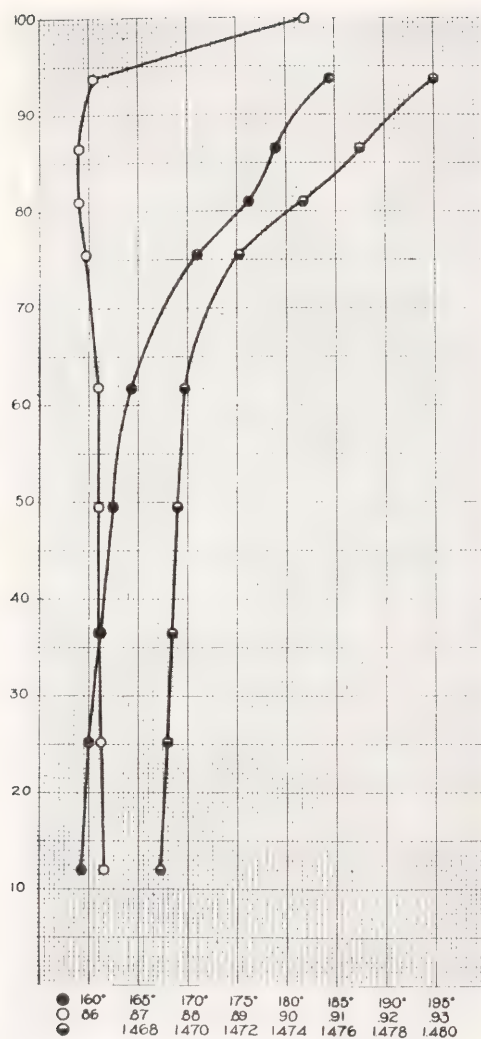


Fig. 24.

Boiling point, specific gravity and index of refraction of "hearts" obtained in refining of crude turpentine No. 1.

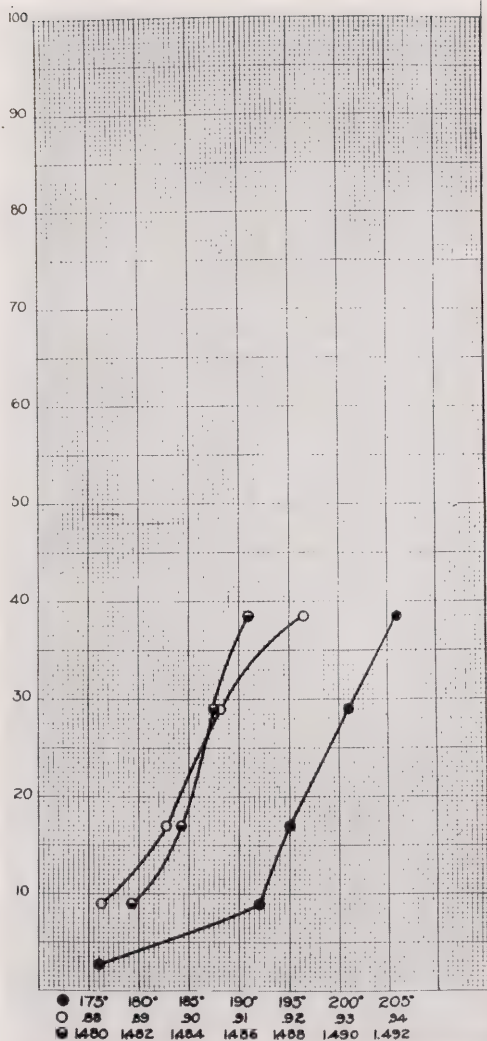


Fig. 25.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 1.

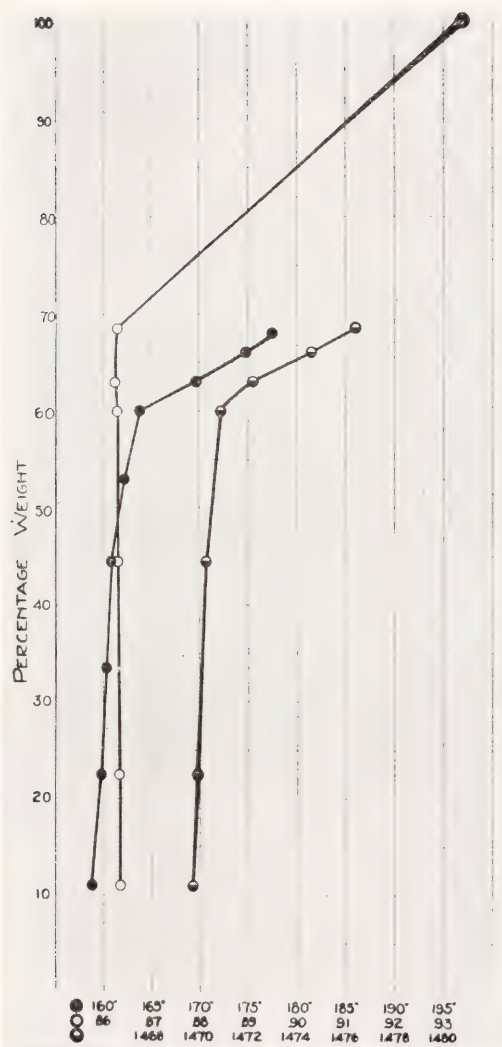


Fig. 26.

Boiling point, specific gravity and index of refraction of crude turpentine No. 2.



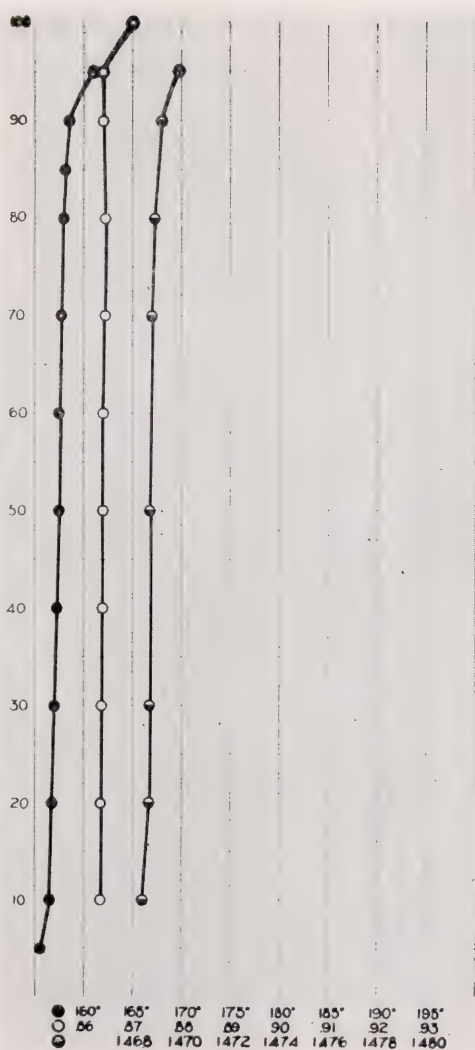


Fig. 27.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 2.

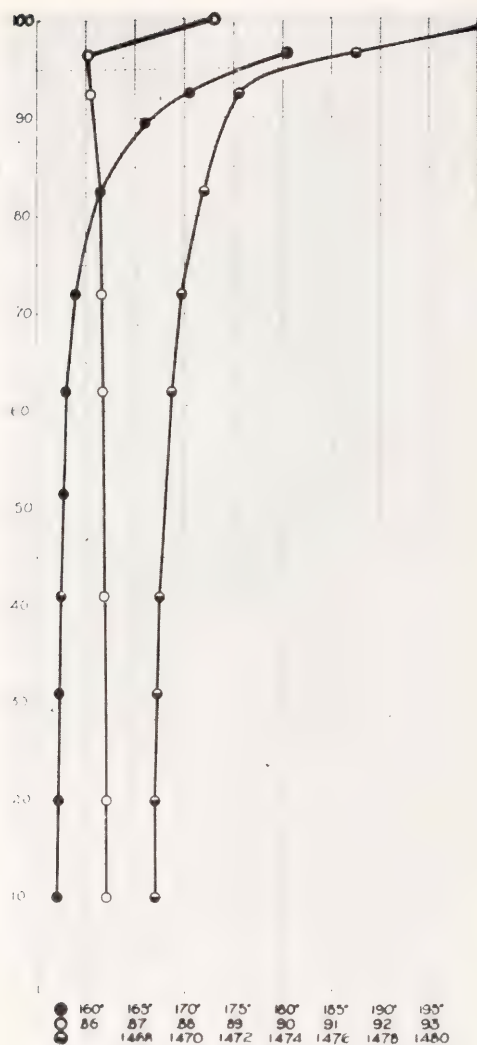


Fig. 28.

Boiling point, specific gravity and index of refraction of "hearts" obtained in refining of crude turpentine No. 2.

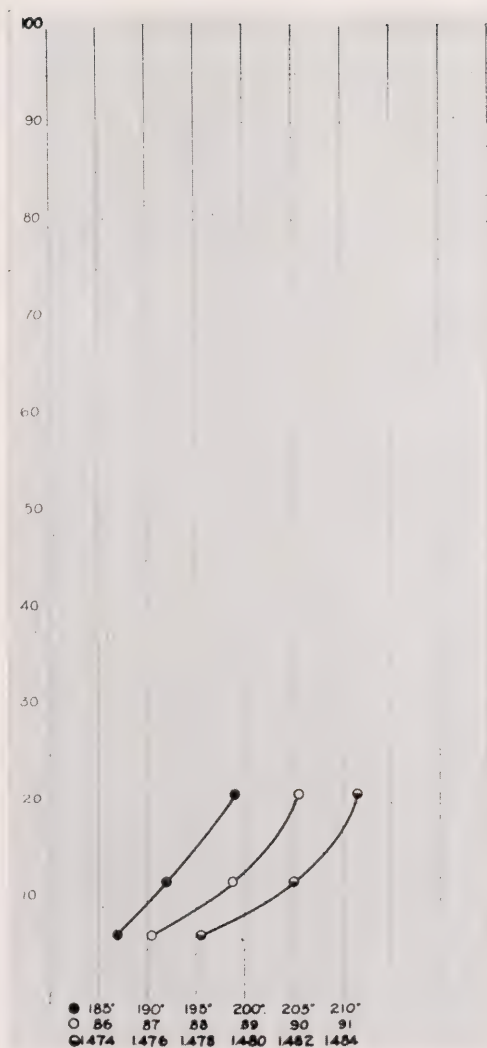


Fig. 29.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 2.

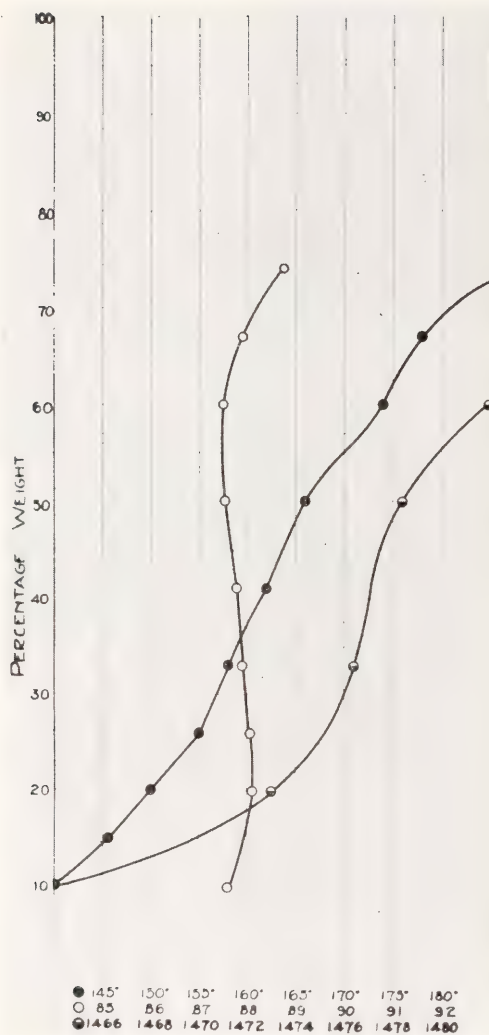


Fig. 30.

Boiling point, specific gravity and index of refraction of crude turpentine No. 3, untreated.

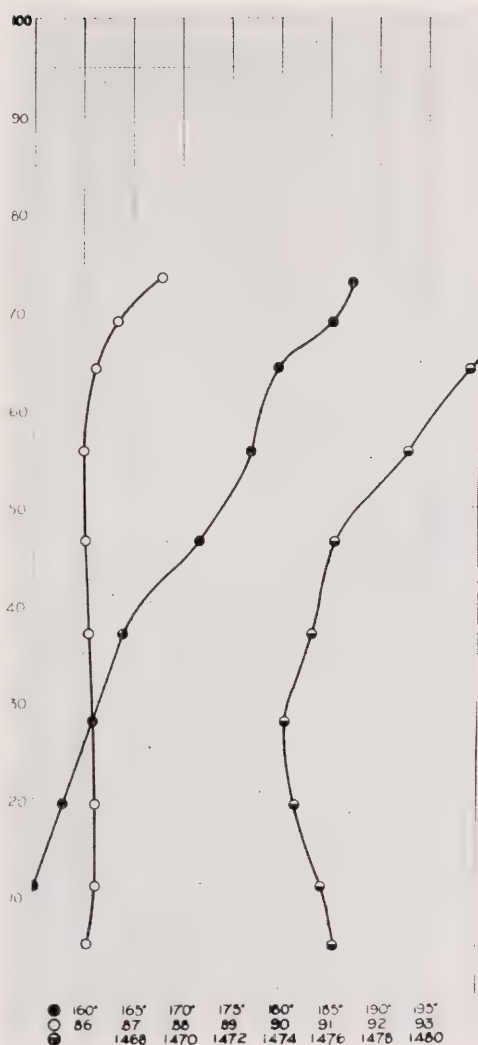


Fig. 31.

Boiling point, specific gravity and index of refraction of crude turpentine No. 3, after treatment with caustic soda solution.



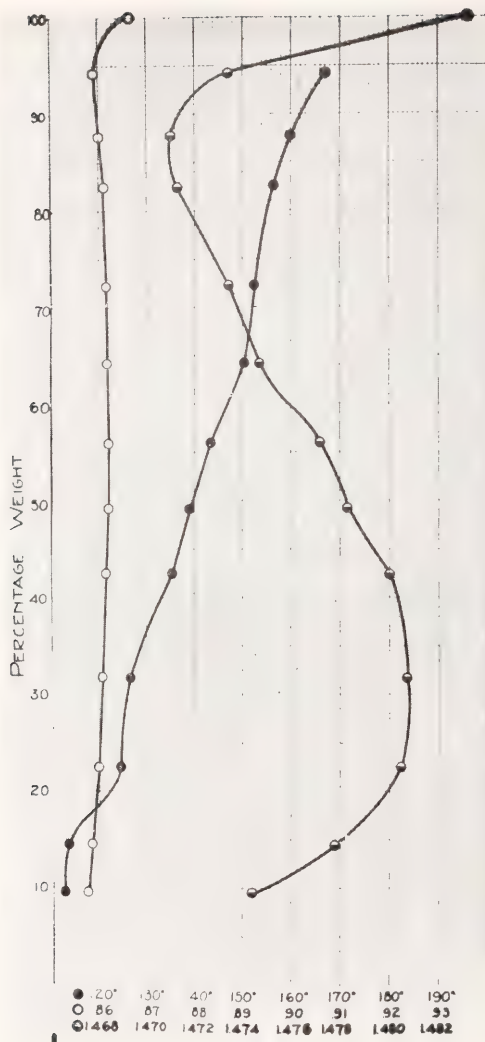


Fig. 32.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 3.

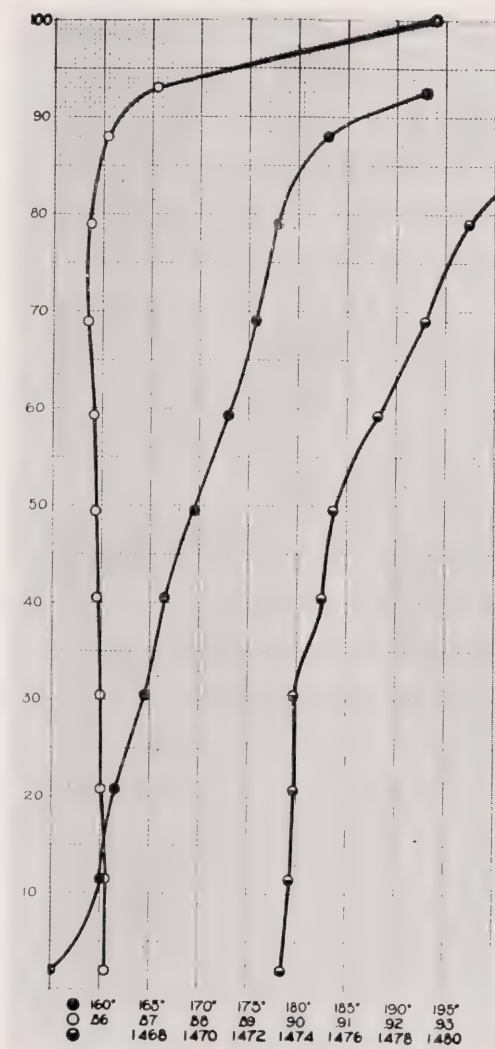


Fig. 33.

Boiling point, specific gravity and index of refraction of "hearts" obtained in refining of crude turpentine No. 3.



Fig. 34.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 3.

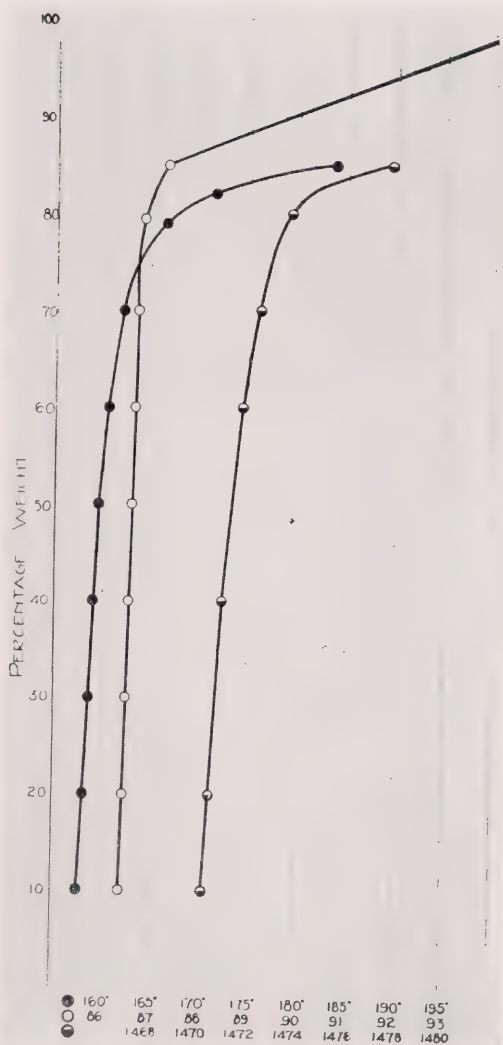


Fig. 35.

Boiling point, specific gravity and index of refraction of crude turpentine No. 4.

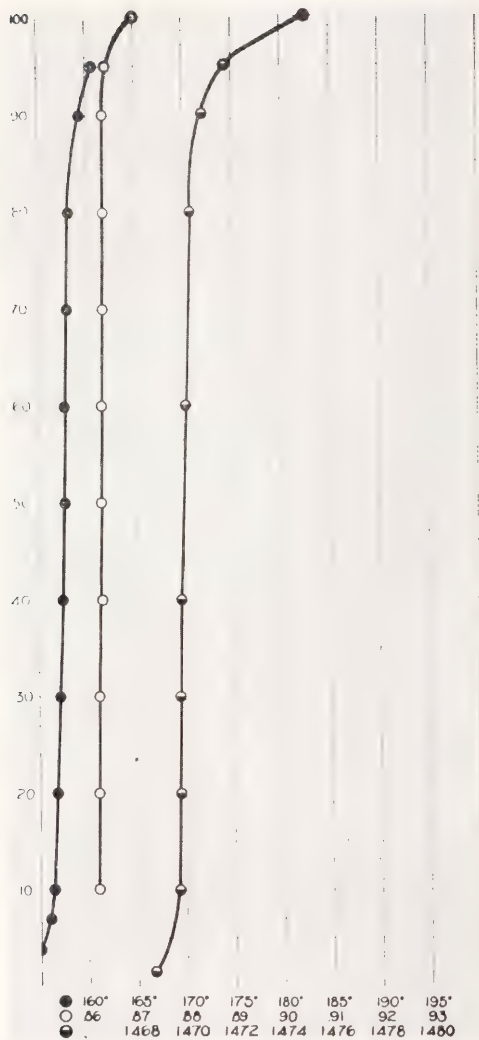


Fig. 36.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 4.



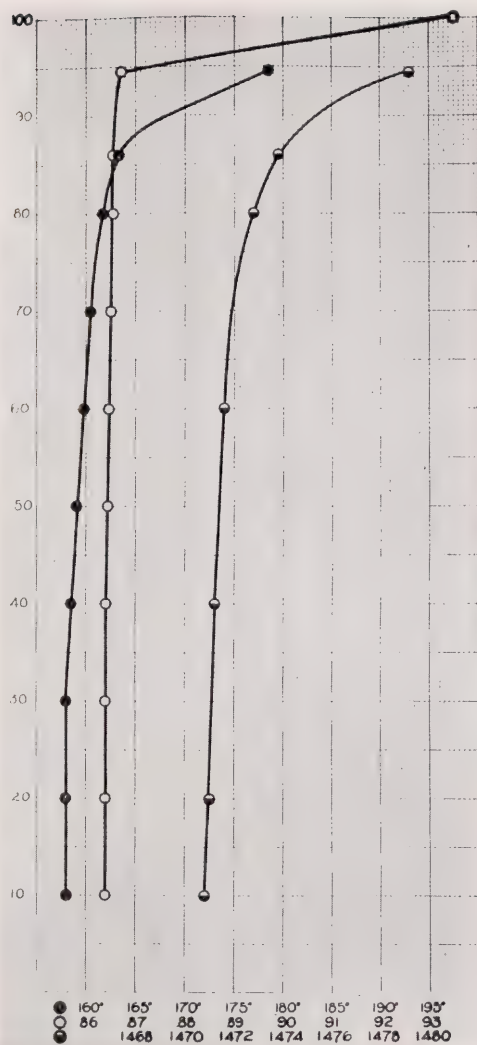


Fig. 37.

Boiling point, specific gravity and index of refraction of 'hearts' obtained in refining of crude turpentine No. 4.

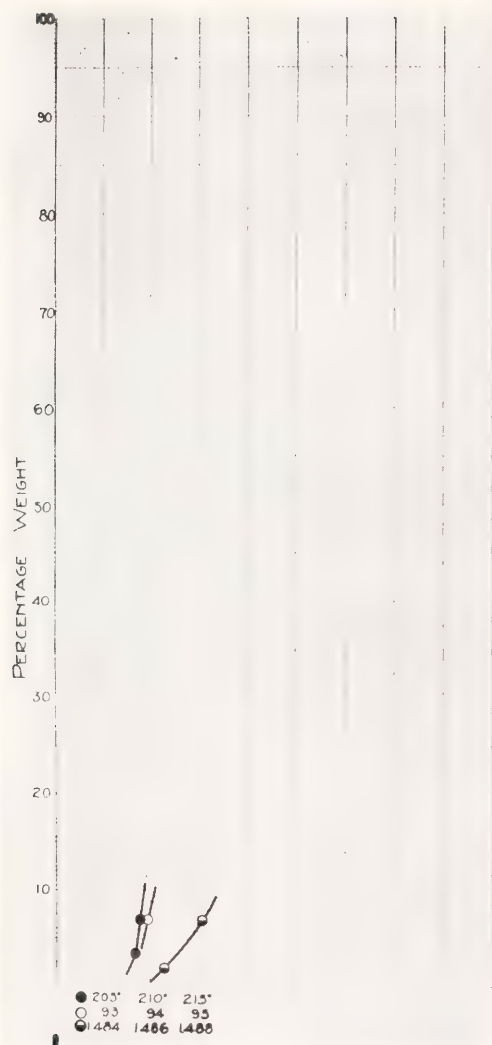


Fig. 38.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 4.

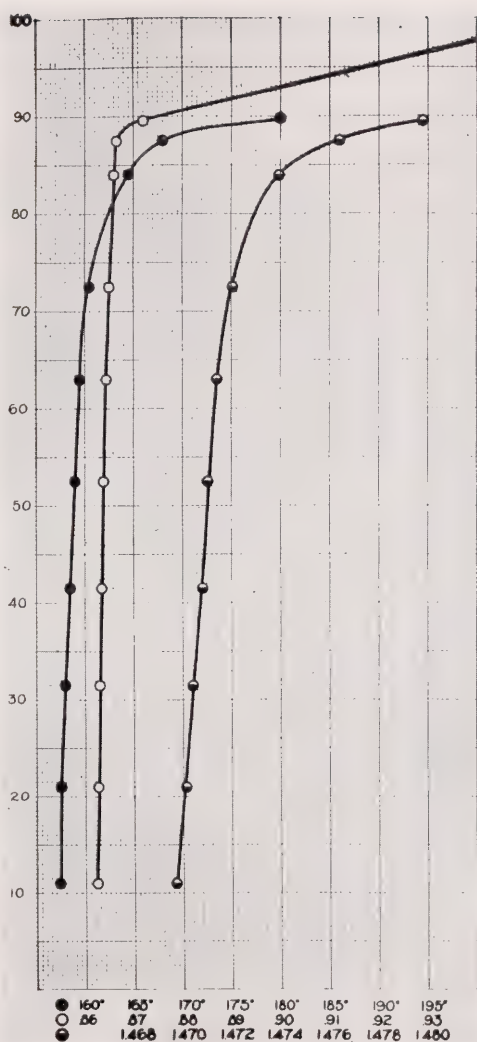


Fig 39.

Boiling point, specific gravity and index of refraction of a commercial wood turpentine refined (Crude No. 4) in an ordinary pot still.

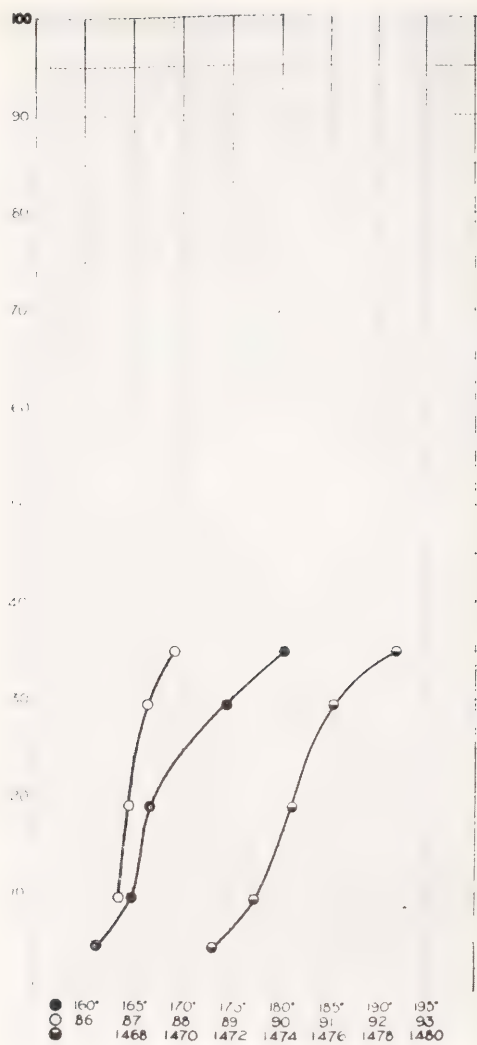


Fig. 40.

Boiling point, specific gravity and index of refraction of commercial pine oil refined in an ordinary pot still.

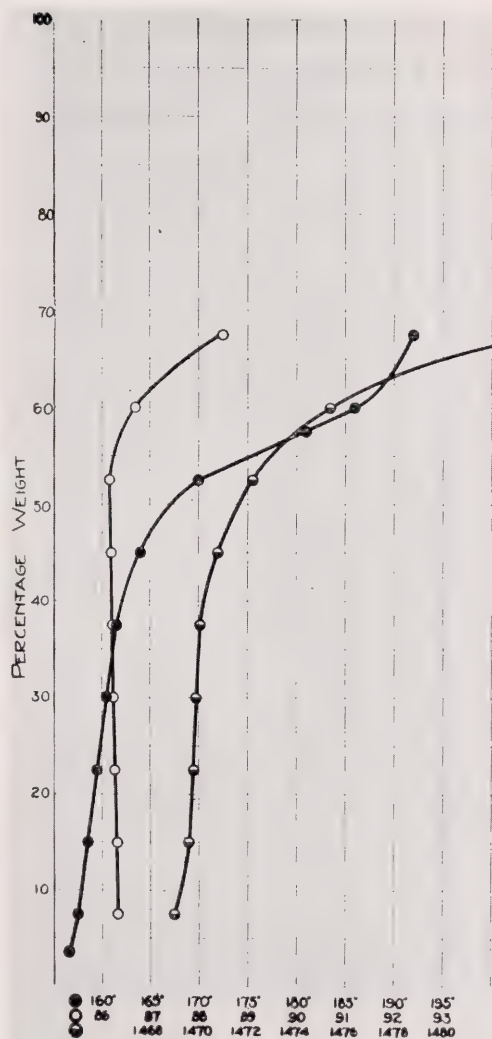


Fig. 41.

Boiling point, specific gravity and index of refraction of crude turpentine No. 5.





Fig. 42.

Boiling point, specific gravity and index of refraction of "heads" obtained in refining of crude turpentine No. 5.

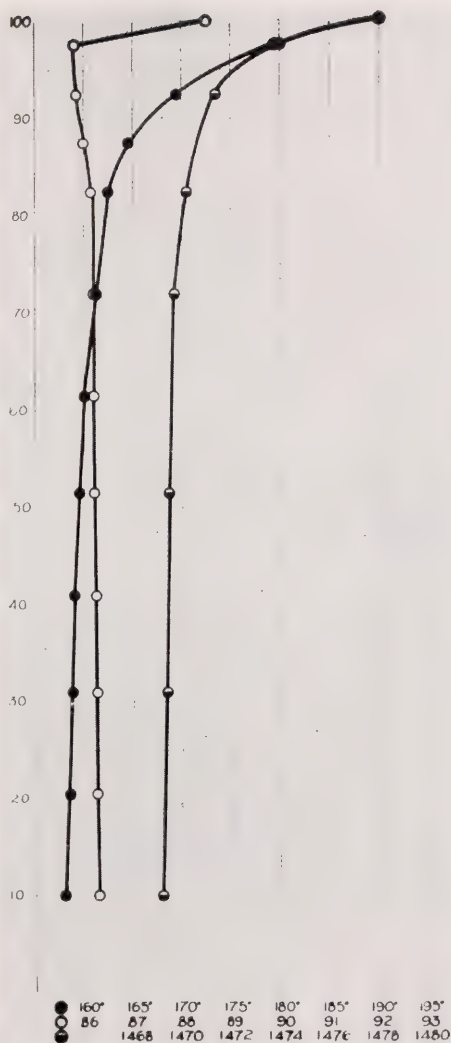


Fig. 43.

Boiling point, specific gravity and index of refraction of "hearts" obtained in refining of crude turpentine No. 5.

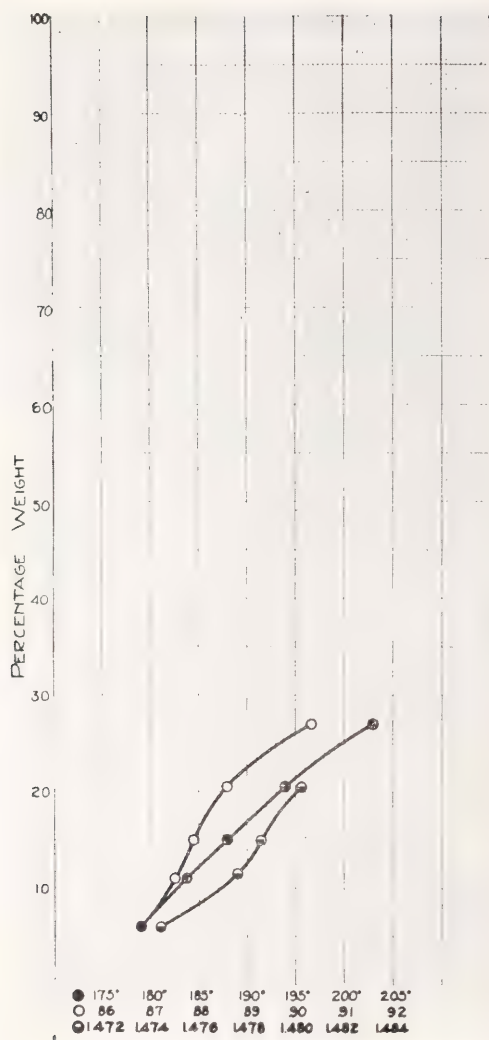


Fig. 44.

Boiling point, specific gravity and index of refraction of "tails" obtained in refining of crude turpentine No. 5.

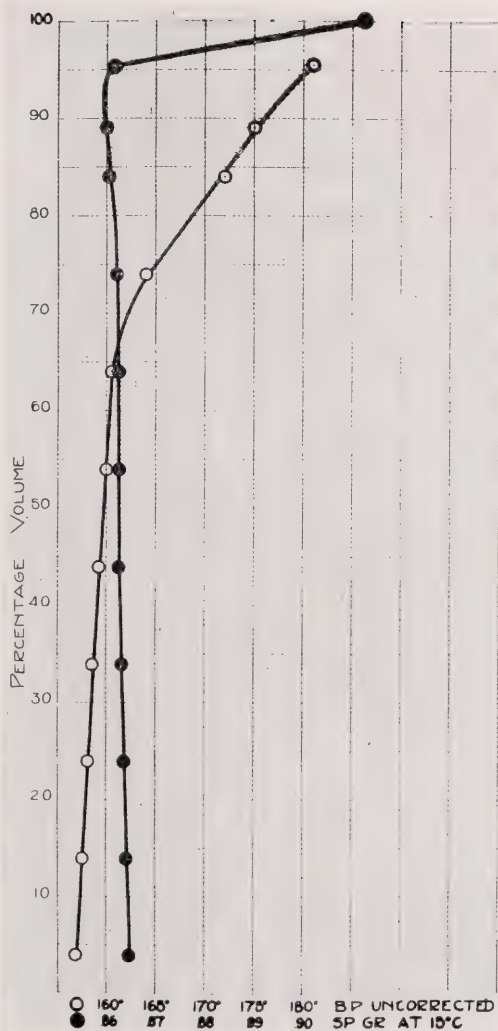


Fig. 45.

Boiling point and specific gravity of turpentine obtained in commercial refining of crude turpentine No. 5.



Fig. 46.

Boiling point and specific gravity of pine oil obtained in commercial refining of crude turpentine No. 5.



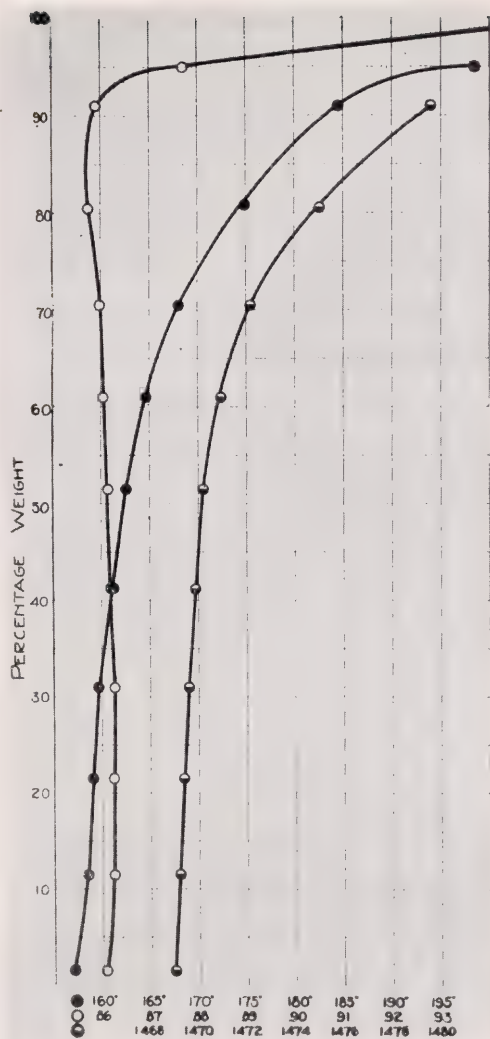


Fig. 47.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 1 analyzed after six months.

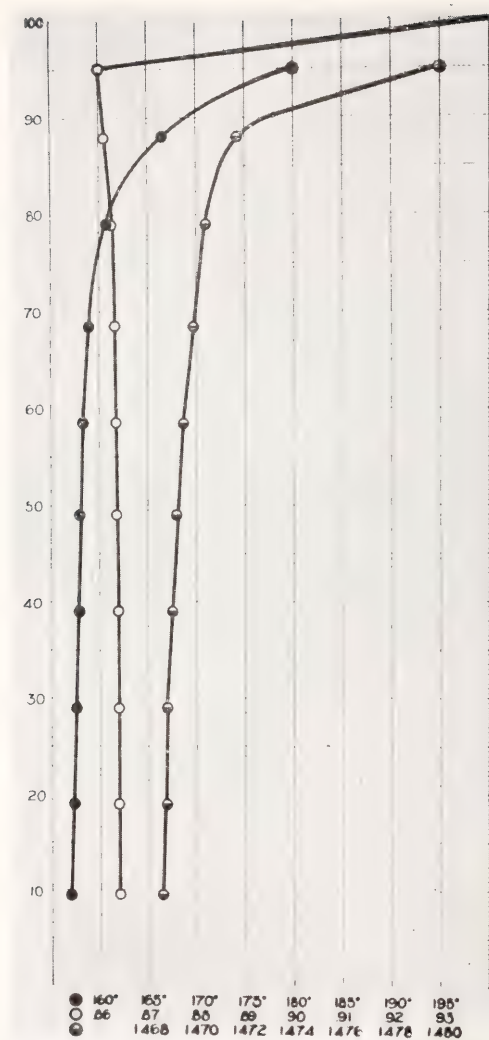


Fig. 48.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 2 analyzed after nine months.

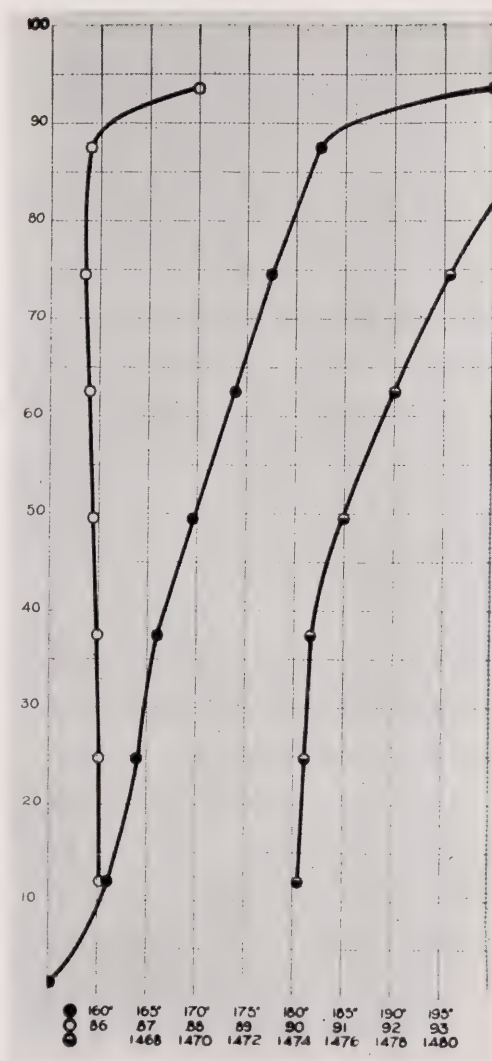


Fig. 49.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 3 analyzed after nine months.

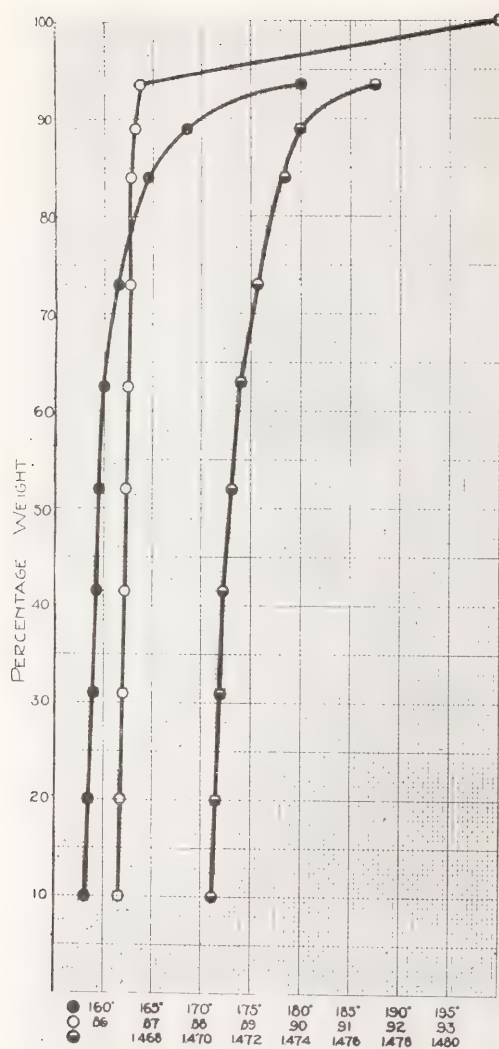


Fig. 50.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 4 analyzed after nine months.

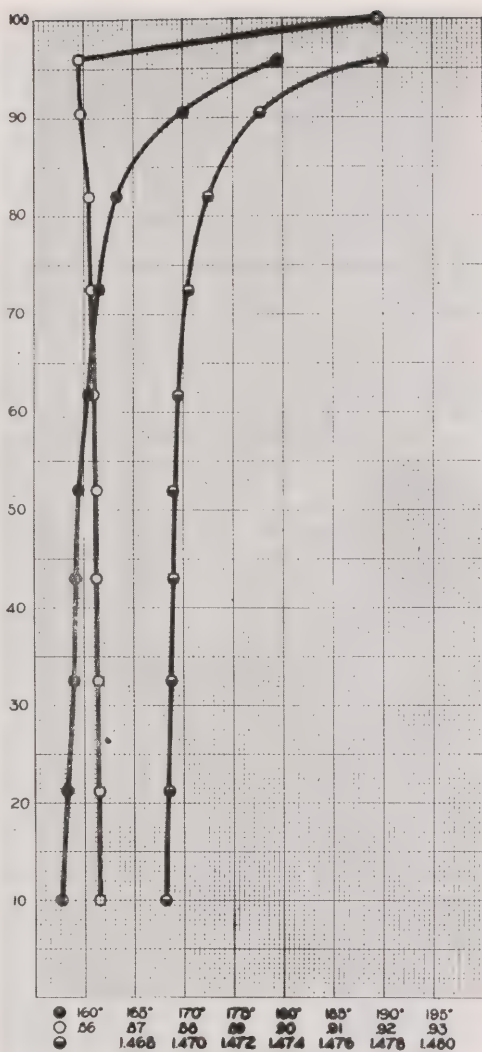


Fig. 51.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 4 analyzed after three months.

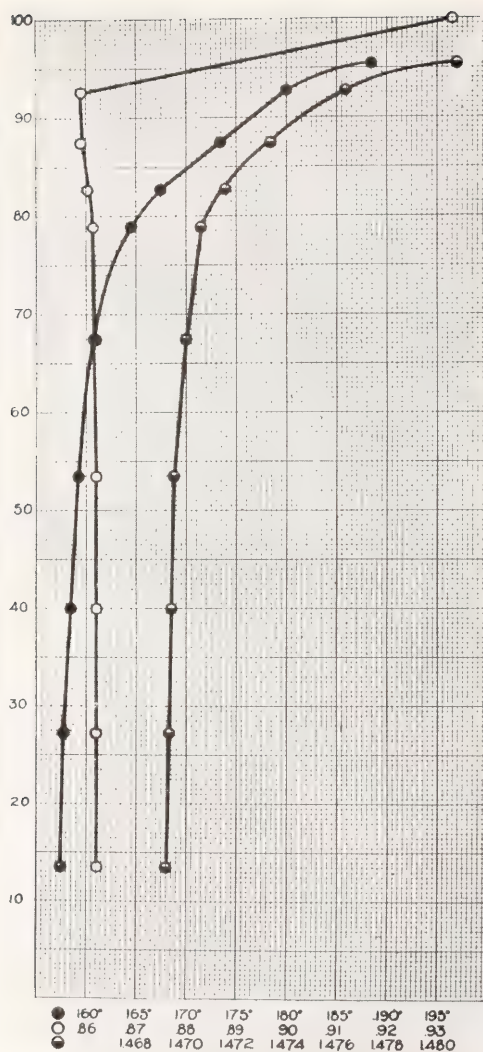


Fig. 52.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 5 analyzed after six months.



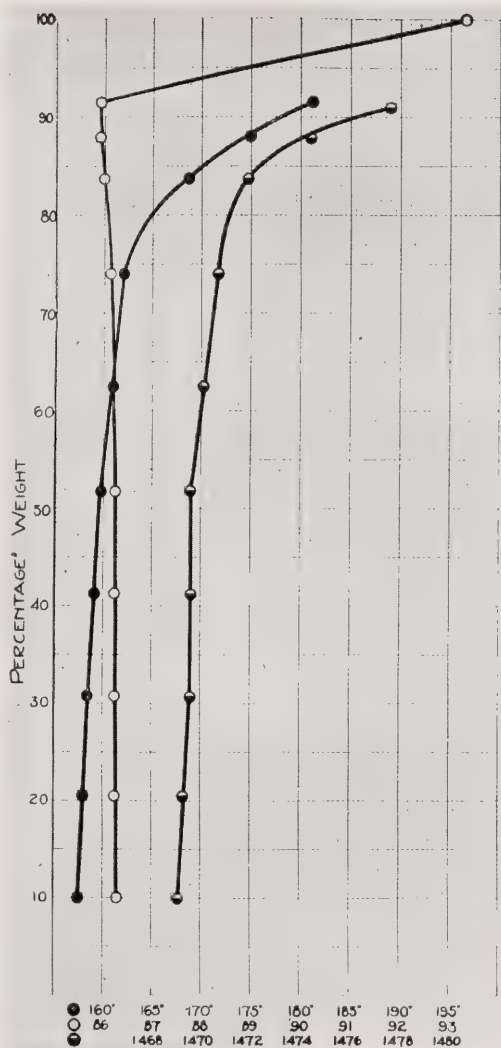


Fig. 53.

Boiling point, specific gravity and index of refraction of the turpentine obtained from crude No. 5 analyzed after ten months.

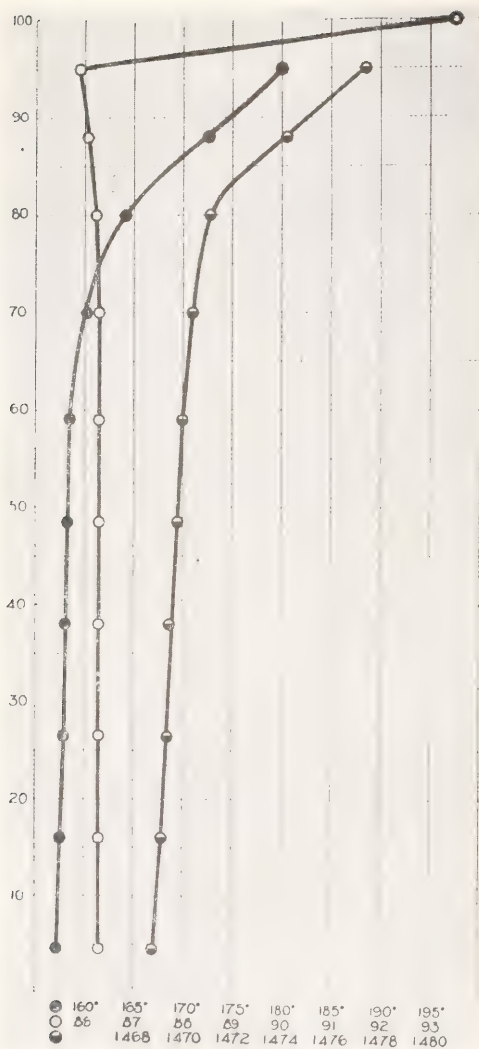
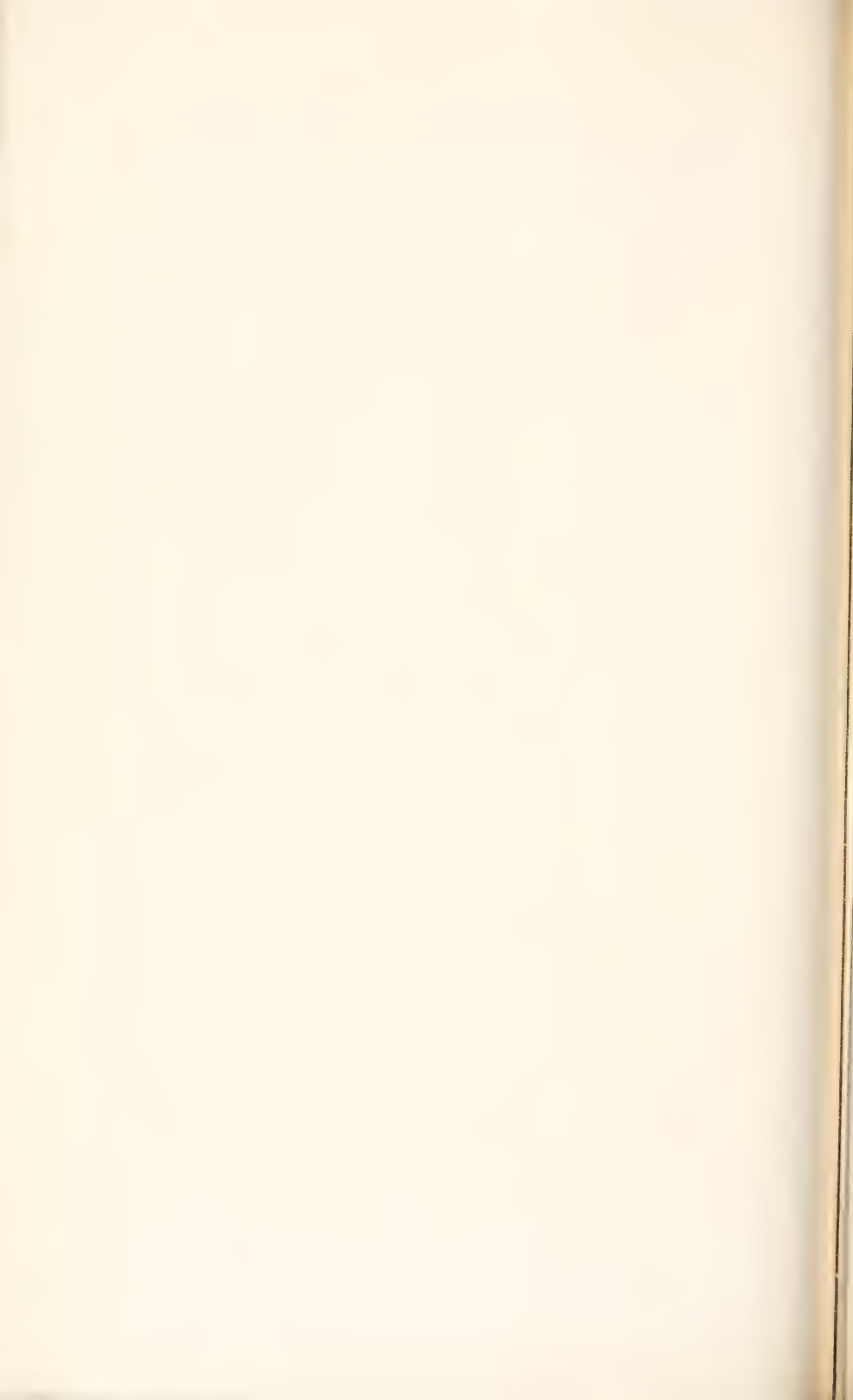


Fig. 54.

Boiling point, specific gravity and index of refraction of turpentine obtained from crude No. 5 after redistillation.





### *Boiling Cap Sections*

The boiling cap section, shown diagrammatically in Figure 15, is the typical and important division of the column, the other kinds of sections being modifications of this typical section. Each section is 14 inches by 12 inches inside diameter, and is supplied with eight boiling caps and two return pipes. The liquid level on each section is kept even with the top of the return pipes, and the vapors from the section below are made to pass through this liquid by means of the boiling caps; the rim of each cap is slotted so that the vapor passes through the liquid in small bubbles, and good contact between the ascending vapor and the descending liquid is thus obtained.

### *Reflux Condenser Sections*

The reflux condenser sections are really a combination of a boiling cap section with a reflux condenser; that is, they are similar to Figure 15 except that below the return pipes there is a chamber filled with copper tubes around which the vapors must pass and through which water is kept flowing.

### *Steam Chamber Sections*

The steam chamber sections are like the boiling cap sections except that they are higher and are furnished with two steam inlets near the bottom, and an opening near the top for connection with the pressure regulators.

### *Outlet Sections*

The vapor outlet sections are simply chambers for covering the top of the last boiling cap or reflux section, and are provided with a suitable opening for conveying the vapors to the condenser.

### *Pressure Regulators*

A sketch of the pressure regulator is given in Figure 16. It consists essentially of two chambers A and B separated by the rubber diaphragm C. Any motion of the diaphragm such as might be caused by a change of pressure in either chamber, is communicated by the system of levers to the steam valve D.

For instance, if there is an increase of pressure in the steam chamber E, there is a corresponding increase of pressure on the bottom of the diaphragm and the diaphragm moves upward, closing the valve D until the pressure is again normal in E.

### *Separators*

The separator, Figure 17, is the same in principle as the ordinary automatic oil and water separator used in practice, but it is made much more compact in order that only a small amount of oil can be retained in it at one time. This apparatus can be made entirely from ordinary iron pipe and pipe fittings. A separator like that shown in the drawing with a total length of 3 feet and with the main tube made of 2 1-2-inch iron pipe was sufficient for the separation of 20 to 23 gallons of refined turpentine from about the same amount of water per hour.

### *Speed Indicators*

The speed indicator,<sup>1</sup> Figure 18, is based on the principle that there is a definite relation between the rate of flow of a liquid through a small aperture, and the pressure of the liquid at the aperture. The liquid, as for instance the refined turpentine, enters the indicator from the separator through A. The only outlet for the liquid is the tube C which may be entered from the top or through the aperture D; this aperture is made small enough so that, with the normal flow of the liquid, it is necessary for the liquid level to rise some distance in the tube B in order that the pressure may be sufficient to make the liquid flow through D at the same rate it enters through A. The height of the liquid level in B is a measure of the rate of flow through D, and the relationship between these factors is obtained by calibration; that is, by measuring the rate of flow from C, while the liquid

<sup>1</sup> This apparatus can be made almost entirely from ordinary iron pipe and pipe fittings. The pipe C should, however, be of brass so that the aperture D may not be changed in size by rusting and of course the tube B must be of glass. The method of fastening the glass tube into the iron parts is shown in the drawing; E is a support of tin plate or other thin, easily shaped, metal soldered to the nipple in order to support the tube B and the packing F; C is a thin layer of litharge and glycerin cement which makes the joint oil or water tight.



level is maintained at constant measured distances above D. The calibration curve for the crude turpentine indicator is shown in Figure 19.

The other parts of the apparatus were of standard design and require no special explanation.

#### *General Arrangement and Operation of Apparatus*

A diagram of the general arrangement of the apparatus is given in Figure 20. The fractionating column A is divided into the two separate columns  $A_1$  and  $A_2$  at the place marked by the heavy line.  $A_1$  and  $A_2$  are made up of the different kinds of sections already described, as follows:  $A_1$  from the bottom upward, one steam chamber section, five boiling cap sections, two reflux condenser sections and one outlet section.  $A_2$  is similarly made up of one steam chamber section, thirteen boiling cap sections, three reflux condenser sections and one outlet section.

The tank for crude oil F is connected through the pump G with the reservoir D; the overflow pipe from D, through valve 9, furnishes an air outlet for D while it is being filled and serves the purpose also of notifying when D is full; the return pipe through valve 10 also makes it possible to draw out any material from D directly into the tank F. The reservoir D is simply a 110 gallon steel drum arranged on the principle of a Mariotte's bottle in order to keep the flow of crude turpentine through valve 1 constant, whatever the level of crude turpentine in D. The reservoir D having been filled, and valve 10 closed, valve 1 is opened until the crude is running at the required speed as registered on the speed indicator J, say 25 gallons per hour. The crude then flows through the feed heater C, where it is heated by steam from valve 2 to a temperature of about 95°C., and enters the upper column  $A_1$  at the fourth boiling cap section as indicated. The steam supply is now adjusted by the pressure regulator  $H_1$ , and the water in the reflux sections by valve 4 so that the distillate leaving the top of column  $A_1$  is running at the required speed as indicated on the speed indicator  $J_2$ . The speed required is determined from the analysis of the crude turpentines; for instance, if 5 per cent of low boiling material which it is desired to remove from the refined turpentine is present in the crude, then

it is only necessary to adjust the speed of the first distillate to 5 per cent of the speed of the crude.

The portion of the crude not distilled in column  $A_1$  flows from the bottom section through the trapped pipe 8 into the column  $A_2$  at the sixth boiling cap section. Here the distillation process is repeated as in the top column, the water and steam supplies being adjusted by valve 5 and the regulator  $H_2$ , respectively, so that the distillate leaves the top of  $A_2$  at the required rate.

The undistilled residue or "tails" runs out in liquid form from the first boiling cap section, is cooled in the tails cooler I, separated from the water, and the speed measured in the indicator  $J_3$ . The speed of the tails is not directly controlled, but is dependent upon the speeds of the other products, being equal to the speed of the crude, minus the sum of the speeds of the two distillates.

A constant head for the water supply is maintained by means of the float valve in the reservoir E so that when the valves 4, 5, and 13 are once adjusted, the flow of water through the condenser B, and therefore through the refluxes of  $A_1$  and  $A_2$  will be constant. The pressure regulators  $H_1$  and  $H_2$  are used to maintain a constant pressure of steam in the bottom section of the columns  $A_1$  and  $A_2$ , respectively, and therefore the speed of the distillates, once properly adjusted, should remain constant. There were in most cases, however, small variations in the speed of the different products during the course of the distillation.

### *Refining of Crude Turpentine No. 1*

#### *Method of Production*

This crude turpentine was obtained from a plant using the destructive distillation process; during the first part of the distillation, however, the retorts are heated slowly, so that, while the crude turpentine is being distilled from the wood, the temperature is kept as low as is readily possible.

#### *Analysis and Chemical Treatment*

The analysis of the crude is given in Figure 21. The odor of the first four fractions was very disagreeable, and the color was a dark yellow; these properties, in connection with the high grav-

ity, indicated the impossibility of obtaining by distillation alone any refined turpentine of good quality from this part of the crude, although the boiling points were mostly within the range of a good turpentine. On account of the probability that the contaminating material could be removed by treatment with alkali, the original crude turpentine was agitated with a warm caustic soda solution until there was no further action.

The analysis of the treated crude is shown in Figure 22. The gravity of the first few fractions was decreased and the index of refraction was increased by the treatment; the color and odor of all the fractions were also improved. The first fraction of the treated crude, however, had a more disagreeable odor and more color than the other fractions; the second fraction had these undesirable qualities, but to a lesser degree; the rest of the fractions were practically colorless and had only slight traces of the strong odor of the first fraction. The fact that the portion of the distillate having the undesirable properties had also boiling points lower than the rest of the material, made it seem possible that the undesirable portion could be separated by distillation, with a consequent improvement in the properties of the refined turpentine.

The heavy oils began to come over in quantity at about 70 per cent and the distillate beyond this point was practically free from terpenes.

### *Distillation*

It was decided therefore to separate this crude turpentine by the refining process into two distilled products and a residue, as follows: (1) "Light oils" or "heads" with boiling points below those of turpentine, 5 per cent; (2) refined turpentine or "hearts," 65 per cent; and (3) "heavy oils" or "tails" with boiling points and gravity above those of turpentine, 30 per cent. In order to secure such a separation in the refining still it was necessary to regulate the flow of the different products to the following speeds (the crude turpentine running at 25 gallons per hour):

For heads 5 per cent of 25 or 1.25 gallons per hour.

For hearts 65 per cent of 25 or 16.25 gallons per hour.

For tails 30 per cent of 25 or 7.5 gallons per hour.

In the distillation of this turpentine and all others as well, the first runnings of the distillates were caught separately until the adjustment was completed, because the composition of the products would be at first very variable. The analyses shown hereafter represent the composition of the products obtained after the still was properly adjusted and running smoothly. For instance, this run on Turpentine No. 1 occupied about four and one-half hours, but the products shown in the analyses were obtained during a little less than four hours of this time.

### *Products of Distillation*

The analyses of the products obtained from the distillation of Crude Turpentine No. 1 are shown in Figures 23, 24 and 25.

*Heads.*—The heads, Figure 23, are seen to be very variable in composition, about the first 70 per cent having higher indices of refraction and lower boiling points than the first fraction of the hearts; this portion of the distillate also had a darker color and more disagreeable odor than the fractions above 70 per cent. That portion above 70 per cent could well be included in the hearts without affecting the properties of the latter but it is probably not possible to separate completely as small an amount of heads as were present in the crude, 2.5 to 3.0 per cent, without removing some of the hearts at the same time.<sup>1</sup>

*Hearts.*—The analysis of the hearts is shown in Figure 24; there is apparently no material in the hearts with boiling points below 158°C., and the color and odor of the first fractions were not markedly different from those of the next few fractions; that is, the separation of the heads from the hearts was complete. This separation of the low boiling constituents improved both the color and odor of the refined turpentine, making it almost colorless and leaving only a faint trace of the "destructive distillation" odor. There was a small amount, about 6 per cent, of heavy material in the hearts, showing an incomplete separation from the tails.

<sup>1</sup> The heads, on account of the method of their production could not contain any heavy oils and the higher physical properties of the residue in this analysis (and in the analyses of all the other heads) must be due to polymerization during the distillation (See page 62.).



*Tails.*—The tails were analyzed (Figure 25) only to determine how good a separation was obtained between the tails and the hearts. All the properties of the first fraction (9 per cent) of the tails were higher than any fraction of the hearts, except, of course, the residue. But since the composition of the distillate was changing rapidly at this point (the curves all slanting decidedly) it is probable that a small amount of this first fraction was composed of material with properties the same as some portion of the hearts; perhaps 3 to 4 per cent of the tails were composed of materials which should have been in the hearts.

### *Refining of Crude Turpentine No. 2*

#### *Method of Production*

This crude turpentine was produced at a plant using "light-wood" as a raw material. The process of distillation was the steam process and was different from the usual steam process only in the small size of the chips and in the steam pressure used, which was about 50 pounds.

#### *Analysis*

The analysis of this crude is shown in Figure 26. There were no evidences in this crude of low boiling material similar to that in Crude Turpentine No. 1, but the odor of the first fraction was quite different from the second, and it was decided to separate a small amount of heads in order to find if the odor of the hearts was improved. This crude turpentine is seen to contain about 60 per cent "pinene," 8 per cent dipentene and 32 per cent heavy oils. It was decided to attempt to obtain about 4 per cent of heads, which would leave about 64 per cent of turpentine material to be separated as hearts.

#### *Distillation*

The crude was run into the still at a speed varying from 24.8 gallons per hour to 25 gallons per hour; the heads were kept as close as possible to 1 gallon per hour (varying from 0.5 to 1.5 gallons per hour) and the hearts varied from 15.7–16.1 gallons per hour. Except for the rather large variation in the heads, the distillation seemed to run smoothly.

### *Products*

The analyses of the products are given in figures 27, 28 and 29.

*Heads.*—Although the difference in odor between the heads and the hearts was quite noticeable, they did not show any great difference in other properties; the odor of the first 10 per cent of the heads was also somewhat different from the rest of the fractions. The amount of material present in these heads with properties different from the main part of the turpentine (hearts) is therefore very small in proportion to the original crude, so small that it is impracticable and really unnecessary to separate it.

*Hearts.*—The hearts contain only about 3.5 per cent of heavy material, and the gravity of this portion is only slightly greater than that of the main part of the hearts, the gravities being 0.885 and 0.863 respectively, which shows a very satisfactory separation of hearts and tails.

*Tails.*—The tails, however, contain a small amount of material which might have been included in the hearts. The properties of the first fraction of the tails (7 per cent) are higher than any portion of the hearts except the residue, but the difficulty of completely separating in one distillation a small amount of turpentine material, from a large proportion of higher boiling material like the "pine oil," and the fact that the properties of the distillate were changing rapidly when this fraction was taken both indicate that there was a considerable proportion of turpentine material present in this first fraction of the tails. Perhaps 5 per cent of these tails were composed of turpentine materials. This is, however, a fairly satisfactory separation, only 5 per cent of 32 per cent, or 1.6 per cent of the original crude, not being properly separated.

### *Refining of Crude Turpentine No. 3*

#### *Method of Production*

This turpentine was obtained from a destructive distillation plant using "lightwood" as a raw material; the distillation process is very similar to that employed by the hardwood retort plants in the North, the horizontal cylindrical retorts holding



about one cord of wood and the complete distillation taking only twenty-four hours. The total distillate is condensed and collected together and the pyroligneous acid removed from the crude oil by settling. The crude oil thus obtained is distilled with steam until nearly all the volatile oil is removed. The crude turpentine used in the refining experiments was a sample of the distillate obtained from the crude oil as above.

### *Analysis and Chemical Treatment*

The analysis of the crude is shown in Figure 30. It can be seen from the curves that this crude is a very complex mixture since none of the properties remain at all constant over any considerable portion of the distillation; a large part boils below the usual boiling point of turpentine, and the specific gravity over the complete range of the distillation is higher than any portion (except the residue) of a refined turpentine should be. All the fractions were also colored and had very disagreeable odors. It was seen therefore that no separation by distillation alone could give any amount of distillate with properties suitable for a refined turpentine, and that a chemical treatment was necessary before refining by distillation. The crude was therefore agitated with caustic soda solution at 55° C. until there was no more action, which is shown by treating a small amount with additional caustic soda at the same temperature without any change in color of the caustic solution resulting.

The analysis of the crude treated in this manner is given in Figure 31. The proportion of material boiling below 155° C. was decreased considerably, the specific gravity of all the fractions was decreased, and the color and odor of all the fractions improved. The index of refraction curve was, however, somewhat irregular, and all the fractions still retained some disagreeable odor. That portion of the distillate between about 11 per cent and 64 per cent was more suitable for a refined turpentine than that above or below and it was therefore decided to separate the treated crude into 11 per cent heads, 53 per cent hearts, and 36 per cent tails.

### *Distillation*

The crude was run into the still at a speed of 25 gallons per hour and the speeds of the heads and hearts were maintained as nearly as possible at 11 per cent of 25 or 2.75 gallons per hour and 53 per cent of 25 or 10.75 gallons per hour respectively. During this distillation great difficulty was experienced in regulating the speed of the products and the effects of this are seen in the composition of the products.

### *Products*

The analyses of the products are shown in figures 32, 33 and 34.

*Heads.*—The heads, Figure 32, contained about 80 per cent of material of complex composition with widely varying boiling points and indices of refraction; the color of this portion was also darker and the odor much more disagreeable than the last 20 per cent. The properties of this last 20 per cent were such that it could well be included in the hearts, that is, the separation of heads from hearts was not complete.

*Hearts.*—As far as the specific gravity and index of refraction of the first fraction of the hearts, Figure 33, are concerned, it would seem that the separation of the heads from the hearts was complete, but the boiling point, the odor and color of this first fraction indicated that a small amount of heads material was present in the hearts. This incomplete separation between the heads and hearts was probably largely due to the variation in the speed of the heads; this speed varied from 3.1 to 2.3 gallons per hour and while the heads were running at 3.1 gallons per hour, some hearts material would be distilled over with the heads, and when the speed dropped to 2.3 gallons per hour some heads material would escape in the returns from column  $A_1$  to column  $A_2$  and thus get into the hearts. The hearts also contained probably more heavy material with boiling points above  $180^{\circ}\text{C}$ . than is desirable in a well refined turpentine.

*Tails.*—The tails, Figure 34, contain about 5–6 per cent of hearts material showing an incomplete separation of hearts from tails.

*Refining of Crude Turpentine No. 4**Method of Production*

The turpentine plant from which this sample of crude was obtained is operated in connection with a sawmill cutting almost exclusively longleaf pine. The raw material for the distillation consists of all the sawdust normally produced in the mill, together with the waste slabs, edgings, trimmings, etc., the large-sized material being "hogged" before it is conveyed to the turpentine plant. The steam distillation process is used, the maximum pressure in the retorts being 10 pounds.

*Analysis*

The analysis of this crude turpentine is given in Figure 35. This crude is of simple composition in comparison with Nos. 1, 2 and 3, being composed of about 84 per cent of turpentine and 16 per cent pine oil, with no evidences of the presence of any dipentene, or of any heads, except that the odor of the first fraction was somewhat different from the next few fractions.

It was desired to obtain one refined steam distilled turpentine containing comparatively large amounts of pine oil in order that the technical properties of two turpentines similar in composition, except for the proportion of pine oil present, might be compared. It was decided therefore to separate this crude into about 2 per cent heads, 88 per cent hearts, and 10 per cent tails and thus obtain a refined turpentine with more heavy oils than No. 2, the other steam distilled turpentine refined.

*Distillation*

The crude turpentine was run into the still at the rate of 24.8 gallons per hour. The speed of the heads varied from 0.2 to 1.0 gallons per hour with an average of about 0.5 gallons per hour, and the hearts varied from 20 to 23 gallons per hour with an average of about 21.7 gallons per hour.

*Products*

*Heads.*—The analysis of the heads from this run, Figure 36, showed that only a very small amount of material different from

the main portion of the turpentine is present. The first fraction of 1.5 per cent had a slightly lower index of refraction than any of the rest of the fractions, and the odor of the first 10 per cent of the distillate was quite different from the rest of the distillate. As in the case of Crude Turpentine No. 2, however, the amount of this material is so small, and its properties are so slightly different from the rest of the turpentine, that it is unnecessary to attempt to separate it.

*Hearts.*—The analysis of the hearts, Figure 37, showed about 6.5 per cent of pine oil present, as was to be expected from the manner of regulating the distillation.

*Tails.*—The tails, Figure 38, were apparently entirely free from hearts material, the very high values for the physical properties of the first fraction of 6.5 per cent, indicating that only a very small proportion of this fraction could possibly be made up of turpentine material. The separation in this case is therefore very satisfactory, the hearts containing probably no more heavy material than is allowable in a good grade of turpentine, and the tails being practically free from turpentine.

#### *Products Obtained by Commercial Refining Method*

In order to obtain a comparison between the efficiency (as regards completeness of separation) of the column still used in this investigation and that of the ordinary pot still used in practice, samples of the turpentine and pine oil, refined at the plant where this crude turpentine was produced, were obtained and analyzed. The samples were both from the same charge of crude and were refined by a single distillation with steam. The turpentine, Figure 39, is seen to contain about 12 per cent of heavy oils while the pine oil, Figure 40, contains about 30 per cent of turpentine, showing that a very incomplete separation was obtained.

#### *Refining of Crude Turpentine No. 5*

##### *Method of Production*

This crude turpentine was produced from "lightwood" by means of the bath process of distillation. The "lightwood" in cordwood form is loaded on cars and run into the large horizontal



cylindrical retorts, then the hot bath material, pine tar pitch, is circulated through the retort, the "extractor" and the furnaces in the order given. In the furnaces the temperature of the bath material is kept up to the maximum of  $195^{\circ}\text{C}$ . In the extractor live steam is blown through the bath to remove the volatile oils which are carried by the bath from the retort. These volatile oils constitute the crude turpentine used in the refining experiments.

### *Analysis*

The analysis of this crude turpentine is given in Figure 41. There was no evidence of any heads material in this crude except a slightly different odor in the first fraction; and apparently about 57 to 58 per cent could be obtained which would contain a very small amount of heavy oils. It was decided therefore to attempt to separate the crude into the smallest possible amount—2 per cent—of heads, 55 per cent of hearts and the rest tails.

### *Distillation*

The crude was run into the still at the rate of 25 gallons per hour, and the steam and water were adjusted to give as nearly as possible 0.5 gallons per hour of heads, and 13.75 gallons per hour of hearts; these adjustments were maintained within the usual limits of variation.

### *Products*

*Heads.*—The analysis of the heads thus obtained is given in Figure 42. From the boiling point and index of refraction curves it is apparent that the first 10 per cent of the distillate contains a small amount of material with properties somewhat different from the rest of the distillate, and this was further indicated by the odor of the first fractions. As was the case with Turpentine No. 2 and No. 4, however, it is probable that there is so little of this material present that it is not only impracticable but unnecessary to attempt its separation.

*Hearts.*—The hearts, Figure 43, are seen to be almost free from heavy oils, only about 2 per cent of material with a gravity of .890 being present, and the low gravity and index of the residue indicating that even this 2 per cent is largely composed of sub-

stances similar to the last few fractions of the distillate. A very nearly complete separation of hearts free from tails was therefore accomplished in this run.

*Tails.*—The tails, however, are seen (Figure 44) to contain probably 15 per cent of hearts material, so that the separation of tails free from hearts was not complete.

### *Commercial Scale Refining*

The refining done on the five crude turpentines described above was intended not only as experiments in refining, but also as a study of the composition of crude wood turpentines and the products obtainable from them, and especially as a means of obtaining samples of wood turpentine with known compositions and methods of production, so that these samples might be used in tests to determine the industrial value of wood turpentines of different composition. The best conditions for the different distillations were not studied, the arrangement of the still was not changed throughout the experiments, and only in two cases were the distillations repeated in order to secure better results. It must not be considered therefore, that the best possible results were obtained, or that the most suitable arrangement of the column was used in all cases. The composition of the crude turpentines Nos. 2, 4 and 5, for instance, was such that the separation of constituents with boiling points below those of refined turpentine was not necessary, and instead the production of a refined turpentine and a refined pine oil would have been preferable, but the arrangement of the column was not suitable for the production of these last products, and therefore in no case was a refined pine oil produced.

It will be interesting in this connection to give a brief statement of some of the results obtained in another piece of work in which more nearly commercial conditions prevailed and in which the column was arranged for the production of a refined pine oil as well as a turpentine.

### *Field Work on Crude Turpentine No. 5*

In this work the still was set up at the plant where the crude turpentine No. 5 was produced. The general arrangement of



the still was the same as in the previous work except that the crude reservoir was modified so that continuous long runs could be made and the grouping of the sections was changed so that the upper column,  $A_1$ , contained 13 boiling cap sections and three reflux condenser sections while the lower column,  $A_2$ , contained only five boiling cap sections and two reflux condenser sections. The refined turpentine was distilled from  $A_1$  and the refined pine oil from  $A_2$ . (See Figure 20) The analyses of the products obtained from one run shown in figures 45 and 46 give a good idea of the separations obtained under these conditions; the turpentine contained about 4 per cent pine oil, and the pine oil contained about 2 per cent turpentine.<sup>1</sup> This seemed to be about the limit of the completeness of separation possible, since with larger proportions of pine oil in the turpentine, the amount of turpentine in the pine oil decreased, and vice versa.

Another point of interest obtained in this piece of work was on the test for determining the proper control of the distillation; the control of the still by the specific gravity of the products rather than by the speed of the products was found to be very easy. In this case where the specific gravities of the two constituents to be separated were so different, (say, 863 and 945) such a method of control was very delicate, but in a case like the distillation of crude turpentine No. 3 where two products (heads and hearts) with gravities very nearly the same are to be separated this method would not be applicable.

<sup>1</sup> It will be noticed that figures 45, and 46 are different in many ways from the distillation curves shown previously; index of refraction curves are not given, the boiling point values are uncorrected, and the percentages are by volume and not by weight. These represent the results from such analyses as can be obtained with apparatus which is readily transportable and which can be set up and used without many of the conveniences of the ordinary chemical laboratory. Two 50 c.c. cylinders graduated to 1 c.c. and one 500 c.c. measuring flask can take the place of the more delicate balance in determining the percentages of distillate, and for rough field work the refractometer and barometer can be dispensed with; otherwise the method is the same as previously described. For many purposes a simpler method of this kind is entirely sufficient but for close, careful work the refinements mentioned in the description of the method on pages 66-68 are necessary.

### *Summary of Results of Refining Experiments*

The crude turpentines described above are sharply divided into two groups according to their composition, and the methods used in their production. The methods necessary for their proper refining naturally follow the same grouping, which is as follows:

Group 1. Includes crude turpentines Nos. 2, 4, and 5 which were produced at temperatures below 200° Centigrade.

Group 2. Includes crude turpentines Nos. 1 and 3 which were produced at temperatures above 200° Centigrade.

The following conclusions have been reached for the refining of crude wood turpentines like those of Group 1:

1. A fractional distillation without chemical treatment is sufficient for the production of good grades of turpentine and pine oil.

2. The separation of light oils with boiling points lower than those of the turpentine, is unnecessary.

3. Better separation of the turpentine from the pine oil or, in other words, a greater purity of the final products is obtained with a column still than with an ordinary pot still.

In the refining of crude wood turpentine like those of Group 2, the following conclusions apply:

1. A chemical treatment is required before a distillation can produce a good grade of refined turpentine.

2. The color and odor of the refined turpentine obtained from the chemically-treated crudes by distillation are much improved by the separation of the "light oils" with boiling points lower than those of the turpentine.

3. Although no data are given here to show the results obtained in an attempt to separate the "light oils" by distillation in an ordinary pot still yet it is probable such a separation could not be made successfully.

### COMPOSITION OF WOOD TURPENTINES

Nearly all the experimental work done in connection with this investigation has already been recorded in the previous pages and this division will consist mainly in correlating and discussing some of the data already given, together with information along the same line from other sources.

### *The Relations Between Composition and Methods of Production*

If the crude turpentines are arranged according to the maximum temperatures of their production, the order would be Nos. 4, 2, 5, 1 and 3 (See description of methods of production under each crude turpentine.) The proportion of dipentene in the refined turpentines prepared from these crudes increases in the same order as the maximum temperatures of production (See Figs. Nos. 37, 38, 43, 14 and 33). The comparison of the maximum temperatures with the proportion of dipentene in the *crude* turpentines would have been perhaps more proper, but the analyses of the crude turpentine do not in all cases indicate the proportion of dipentene present, as for instance, in Crude Turpentine Nos. 1 and 3, Figures 21 and 30.

As would be expected also there is a relation between the maximum temperatures and the amount of "light oils" (with boiling points below 157° C.); in Crude Turpentines Nos. 1 and 3 produced at (unknown higher temperatures, light oils are present).

A similar relation also holds between the maximum temperatures of production and the amount of products removable by treatment with caustic soda. These relations between composition and temperature of production are given in tabulated form below:

Table 2. Relations between composition and temperature of production for crude wood turpentines

| Crude Turpentine No. | Maximum Temperature of Production | Dipentene in Refined Turpentine | Light Oils Boiling Point Below 157° C. insoluble in NaOH | Oils, Soluble in NaOH |
|----------------------|-----------------------------------|---------------------------------|--|-----------------------|
| 4                    | 116° C.                           | Practically none <sup>1</sup>   | None   | None                  |
| 2                    | 148° "                            | About 10%                       | "  | "                     |
| 5                    | 195° "                            | " 15%                           | "  | "                     |
| 1                    | High                              | " 25%                           | About 3%   | Some                  |
| 3                    | Higher                            | " 40%                           | " 11%  | More                  |

<sup>1</sup> For a more probable reason than difference in temperature for the smaller amount of dipentene in Turpentine No. 4 see page 83.

*Comparison with Composition of Gum Turpentine*

Before this comparison can be made it will be necessary to add a few words on the composition of gum turpentine to supplement Figure 2. A study of the variation in composition of gum turpentine now in progress in the Forest Products Laboratory indicates that the volatile oil freshly distilled from the oleoresin obtained by chipping live trees of longleaf pine, contains only very small amounts of heavy oils (with gravity above .875). Therefore the 5 per cent of heavy oils shown in Figure 2 are probably due to a partial oxidation of the terpenes in the original freshly distilled oil. Except for the presence of these heavy oils, Figure 2 may be considered as representing the composition of a typical gum turpentine; the only difference between this and other gum turpentine would be in the range of the values for the physical properties of the fractions; in some cases the range of values would be slightly lower; in others, slightly higher.

*Heavy Oils*

The volatile oil obtained by the distillation of pitchy wood from the long leaf pine contains, however, considerable quantities of heavy oils (See analyses of the crude turpentine.) and the presence of these in refined wood turpentine is, therefore, very probable because complete separations of heavy oil from turpentine can not be made even with an efficient column still. Even less perfect separations can be made with the pot stills commonly used, and there is a natural tendency on the part of the refiner to increase the proportion of refined turpentine which can be obtained from the crude turpentine by increasing the proportion of heavy oils in the refined product.

The usual presence of heavy oils in wood turpentine and their usual absence in gum turpentine is then the first difference between these two classes of turpentine. Even in an old gum turpentine which does contain heavy oils (like Fig. 2) it is probable that the composition of these heavy oils is different from those in wood turpentine (See section on Heavy Oils, page 88).



### *Dipentene*

The presence of dipentene in many wood turpentine and its absence in gum turpentine is another possible difference. The refined turpentine obtained from four of the five samples of crude turpentine described contained dipentene and it is probable that most wood turpentine will contain appreciable amounts of this substance. In some seventy-five samples of gum turpentine which have been examined in the Forest Products Laboratory no dipentene has been detected by the method of analysis used. It appears that the presence of dipentene in wood turpentine is not entirely due to the temperature to which the turpentine is subjected, because most gum turpentine have been subjected to temperatures of at least 150° C. during their distillation, and yet crude turpentine No. 2 which was produced at 50 pounds steam pressure (148° C.) contained considerable quantities of dipentene. Dipentene was also found in the volatile oil distilled from lightwood by steam at atmospheric pressure.<sup>1</sup> The influence of temperature is indicated by the increased amounts of dipentene in wood turpentine produced at high temperatures. The dipentene in wood turpentine may then come from two sources, (1) from the dipentene present in the volatile oil as contained in the wood and (2) from the transformation of some of the "pinene" into dipentene by the high temperatures used in the distillation.<sup>2</sup>

### *Light Oils*

The presence of "light oils" in the wood turpentine produced at higher temperatures is another possible difference. It is possible to refine a crude turpentine containing light oils so that the refined turpentine shall be free from light oils (as in the case of crude No. 1) but the separation is difficult and can not readily be made without some kind of a fractionating column. If light

<sup>1</sup> Distillation experiments at Forest Products Laboratory, the report on which has not yet been published.

<sup>2</sup> The absence of noticeable amounts of dipentene in Turpentine No. 4 may be explained from its source—green sawmill waste; that is, old, dead, lightwood or stumps may contain dipentene while green freshly cut timber, may not. It is expected that these debatable points will be settled by some work now under way in this laboratory.

oils are present in the crude turpentine small amounts are liable to be found in the refined turpentine.

### *Rosin Oils*

The fourth possible difference between wood and gum turpentines is difficult to describe since it does not greatly affect the physical properties expressed in the distillation curves. For instance, in the analysis of refined turpentine No. 3 (Figure 33) it was quite noticeable that the odor and color of all the fractions were different from the similar fractions of other turpentines. Except for the small amount of "light oils" present (See p. 87) the peculiar odor and color apparently did not tend to concentrate either in the first or last fractions, but were distributed rather evenly throughout the distillate. These properties were therefore probably due to the presence of some materials other than terpenes, with boiling point, gravity, and index of refraction not much different from the terpenes, the only very strong indications shown in the distillation curves of the presence of materials other than terpenes being in the high index of refraction of the first 30 per cent. From the method of production of this turpentine these other materials can only be high temperature decomposition products of wood fiber or of rosin. Decomposition products of wood fiber could not be present in very appreciable proportion because it is known that the oils from this source insoluble in caustic soda, with boiling points  $155^{\circ}$  to  $180^{\circ}$  and gravity in the vicinity of .85 to .87, are extremely small in amount. It is known, however, that from the destructive distillation of rosin yellow oils answering these requirements can be obtained; the odor of these rosin oils (rosin spirits, rosin naphtha) is very similar to the fractions of this destructively distilled wood turpentine and it is very probable that the peculiar characteristic odor and color of destructive wood turpentines are due largely to the presence of "rosin spirits."

These comparisons of composition have shown that most wood turpentines will be sufficiently different in composition from gum turpentines so that the method of analysis used in these investigations will readily distinguish between them; a wood turpentine produced from green timber at such low temperatures that no



dipentene is formed and so refined that no heavy oils are present is, however, very similar to a gum turpentine. That is, the terpenes present in the wood from a freshly-cut longleaf pine tree are very similar to the terpenes in the oleoresin obtained by chipping the live longleaf pine tree. The boiling point, the specific gravity, and the index of refraction curves from the two turpentines are not very different, but in general these properties seem to be slightly lower in the fractions from the wood turpentines (Compare Figures 2 and 37.). This difference is, however, not great enough to provide a sure means of distinguishing between the two kinds of turpentines since a gum turpentine with especially low values for the physical properties might be almost the same as a wood turpentine with especially high values. It is probable, therefore, that the same constituents are present in each but that more of the higher boiling and higher gravity terpenes are generally present in the gum turpentines.

### *Odor*

There is a considerable difference in odor between the gum turpentines and the wood turpentines even between these which are nearest alike in composition, but in most cases this difference in odor is not due to differences in the main constituents present. For instance, in the refined turpentine from No. 4 it is very probable that the main constituents are the same as in the gum turpentine shown in Figure 2, and yet there was a decided difference in the odor of these two turpentines. Even the presence of dipentene does not entirely account for the difference in odor between wood and gum turpentines, it being noticeable that refined turpentines No. 2 and No. 5, both of which contained considerable quantities of dipentene, resembled gum turpentine in odor more than the products from No. 4 which was more nearly like gum turpentine in composition. It seems likely, therefore, that the distinctive odor of many wood turpentines is due to some material which occurs in so small a quantity that its presence is not readily indicated in any other manner than by the odor. The odor of a wood turpentine like No. 3 is probably due to the presence of rosin spirits, as mentioned on page 84.

*Effect of Differences in Composition on Technical Properties*

Since the reports on the industrial values are not included in this bulletin, it may be necessary to correct the impression in regard to the value of wood turpentine which has perhaps been given by the above discussion. The chief valuable properties of turpentine are usually considered to be its volatility, its solvent power, and its "drying" properties.

*Volatility.*—The volatility of wood turpentines would probably not be greatly affected by the differences in composition mentioned above, this property being measured approximately by the range of boiling points of the various constituents. Large quantities of heavy oils would of course decrease the volatility, but it is doubtful whether the effect of small quantities up to 10 per cent would be noticeable in practice.

*Solvent Properties.*—It is very probable that the solvent properties of dipentene are quite similar to those of "pinene" since these terpenes are so much alike in other respects; the solvent properties of the other materials which do not occur in gum turpentines but which may be present in wood turpentine are probably sufficiently similar so that the small proportion of these which may be present does not appreciably effect the solvent properties of the mixture.

*Drying Properties.*—In drying properties dipentene is apparently equal to "pinene" since it has been found that the time required for drying a mixture of dipentene and linseed oil is the same as for drying a similar mixture of "pinene" and linseed oil.<sup>1</sup> In the case of the drying properties also it is possible that small amounts of rosin spirits, light oils or even heavy oils would not greatly affect the value of the turpentine. Until further data are available on the relation between the composition and industrial value of turpentines, the differences in composition between wood and gum turpentine should not be considered as necessary indications of corresponding differences in value.

<sup>1</sup> Unpublished Mss. on "Terpenes as Oxygen Conveyors," by Edward Kremers.

*Changes in Composition after Refining*

The analyses of the refined turpentines given above in the description of the refining work were made within a few days after the refining. These samples were all kept for considerable periods afterward, some being stored in glass carboys and others in wooden barrels or iron drums, and analyses were made from time to time in order to determine if any changes in composition had taken place. Since the methods of storage were not the same in all cases the results are not accurately comparable either with each other, or with ordinary commercial conditions of storage, but they do indicate, however, the kind of changes and the possible amount of such changes which may take place during storage.

Refined Turpentine No. 1, the original analysis of which is shown in Figure 24, was analyzed again after six months. (See Figure 47.) The only change which had taken place in this time was an increase in the amount of heavy residue from about 6 to 10 per cent; the odor and color had not been appreciably affected.

Refined turpentine No. 2 (original analysis Figure 28) was analyzed again after nine months (See Figure 48.); during this period the heavy residue had increased from 3.5 per cent with a gravity of .885 to 5.5 per cent with a gravity of .94. Otherwise the sample seemed to be unchanged, still being colorless and with no appreciable change in odor.

Refined turpentine No. 3 (original analysis Figure 33) was analyzed after a period of nine months (See Figure 49.); no indications of change in composition were observed.

Refined turpentine No. 4 (See Figure 37.) was analyzed after a nine months' period (See Figure 50.); no apparent change in composition had taken place meanwhile.

Refined turpentine No. 5 (See Figure 43.) was analyzed again after three months (Figure 51); during this short time the amount of heavy residue had increased from 2 per cent with gravity of .885 to 4 per cent with gravity of .92. Other analyses were made six and ten months (figures 52 and 53, respectively) after the original analyses; the amount of heavy residue increased gradually with the time. At the time of the last analysis a considerable yellow color had developed in this sample, perhaps from the

natural process of "aging" or more likely by contamination from an incompletely cleaned iron drum in which it was stored during a part of the time. In order to remove this color and also part of the heavy residue the sample was redistilled with steam in a small laboratory still without a fractionating column; the composition of the redistilled turpentine is shown in Figure 54.

### *Composition of Heavy Oils in Wood Turpentine*

The presence of considerable quantities of heavy oils in the crude wood turpentine produced by steam distillation (See Analyses of crude turpentine Nos. 2 and 4, figures 26 and 35) indicates that some heavy oils occur in the wood as such and are not formed during the distillation process. Experimental work on the steam distillation of longleaf pine has further confirmed these indications since it was found that the proportion of heavy oil in the crude turpentine did not seem to be directly influenced by the temperatures of the distillation.

In the usual commercial refining practice these heavy oils are distilled over after the turpentine and are marketed without further treatment as "pine oil." It was probably a sample of this "pine oil" which was examined by Schimmel and Company,<sup>1</sup> who identified the following bodies:

$\alpha$ -pinene,  $\beta$ -pinene (nopinene), camphene,  $\iota$ -limonene, dipentene, cineol, fenchyl alcohol, camphor, borneol, methyl chavicol, and  $\alpha$ -terpineol. The first six of these, on account of their low boiling points (all below 177° C.) are to be considered as normal constituents of the refined turpentine<sup>2</sup> which, however, occurred

<sup>1</sup> Semi annual Reports April, 1910, page 100.

<sup>2</sup> With the exception of limonene and cineol, these low boiling constituents have been indicated as probable constituents of wood turpentine by the distillation curves previously shown (See p. 15 especially).

On account of the similarity between the two substances limonene could not be distinguished from dipentene by its effect on the distillation curves. Therefore limonene might have been present in any of the wood turpentine which contained dipentene. Cineol, however, has a considerably higher gravity (.930) and a lower index of refraction (1.458) than dipentene and a boiling point (176°-177° C.) which is near enough to that of dipentene so that the two would occur in the same fractions. It is probable therefore that very large quantities of cineol could not have been present in those turpentine whose distillation curves show a decreasing gravity and increasing index of refraction between 170° and 180°.



in the "pine oil" on account of incomplete separation in the refining.

The last five constituents have boiling points above 200° C. and may be considered as normal constituents of "pine oil" although, of course, small amounts of these substances may be present in the refined wood turpentine. (See page 82.)

Since none of these five substances are known to be produced by the rapid oxidation of "pinene" or of the other terpenes in turpentine it is probable that the composition of the heavy oils in a wood turpentine (due to incomplete separation in refining) is not the same as those in a gum turpentine (produced by atmospheric oxidation). (See page 82.)

The heavy oils in destructively distilled wood turpentines probably consist of these same materials together with some decomposition products of the rosin (rosin oils).

#### *Specifications for Wood Turpentines*

It is seen from the above comparisons that specifications for gum turpentine based on the physical properties would not be applicable to all classes of wood turpentine. The presence of dipentene especially would make such specifications inapplicable because dipentene has a lower specific gravity and at the same time a higher boiling point than the terpenes in a gum turpentine. It might also be desirable to have one set of specifications which could include wood turpentines containing small amounts of low boiling material (like No. 3 shown in Figure 33) and such turpentines would certainly be excluded by any specifications based on the properties of gum turpentine.

It is apparent that in the preparation of specifications for turpentine these possible variations in composition must be taken into account and it is probable that some method of examination must be used which will differentiate (1) between high boiling points due to dipentene and high boiling points due to heavy oils; (2) between low gravity due to dipentene and low gravity due to adulterations and (3) between low boiling points due to incomplete separation of light oils and low boiling points due to the addition of substances not normally present in crude

wood turpentine. Such specifications can not be definitely recommended at the present time because there is not sufficient information available on the technical value of wood turpentine of different composition but meanwhile the method of analysis previously described will be of value in determining the composition of wood turpentine and the various distillation curves shown in this bulletin will furnish for comparison a good idea of the variation possible in authentic wood turpentine.

## APPENDIX

### *Practical Tests on Wood Turpentine*

Samples of each of the five wood turpentine, the refining of which is discussed in this bulletin, were submitted to the Paint Manufacturers' Association and to several manufacturers of paints and varnishes for testing. In these tests the sample turpentine were given the same numbers as the crude from which they were distilled. The sample numbers and the numbers of the corresponding text figures, which show the composition of the turpentine at the time they were sent out for test, are as follows:

| Turpentine | Figure showing composition |
|------------|----------------------------|
| No.        | No.                        |
| 1          | 47                         |
| 2          | 48                         |
| 3          | 49                         |
| 4          | 50                         |
| 5          | 54                         |

The reports of the tests are given in full as submitted by the various coöperators. It is not the purpose to make a detailed analysis of the reports for the purpose of drawing conclusions in regard to the use of these turpentine in the paint and varnish industries. This can best be done by those thoroughly familiar with the requirements of these industries. However, the following significant facts are apparent.

1. The lack of concordance between the reports shows the futility of attempting to establish a general relation between the composition and industrial value of turpentine without



standard methods for determining the industrial value. The (individual) reports probably indicate very accurately the relative industrial values of the different turpentines so far as the particular company making the report is concerned, but no general relation is established.

2. Aside from the odor the wood turpentines do not seem to vary much from each other or from gum turpentine; at least the differences between the several turpentines as indicated in any one report are not greater than the differences reported for the same sample by different manufacturers.

3. Although the odor is the property most emphasized in the reports there is no unanimity of opinion on the relative odors of the different samples and in most cases the objection is that the odor is different from gum turpentines rather than that it is inherently objectionable.

The reports follow:

#### REPORT I

"Referring to the samples of turpentine which you sent us October 24th, we have completed the preliminary investigation, and in carrying through the tests, which were made comparatively, we have added to the five samples submitted by you, a sample of regular standard gum turpentine, marked "A" and a sample of our standard wood turpentine which we are regularly using, marked "B." We found the specific gravities to be as follows:

|    |       |
|----|-------|
| A  | .8680 |
| #4 | .8680 |
| B  | .8650 |
| #3 | .8650 |
| #1 | .8650 |
| #2 | .8635 |
| #5 | .8625 |

*Flash Point:*

|         |                     |
|---------|---------------------|
| A and B | (not taken)         |
| #3      | 113 Degrees Fahr.   |
| #1      | 109.4      "      " |
| #5      | 105      "      "   |
| #4      | 103.6      "      " |
| #2      | 101.8      "      " |

*Staining Power:* (on white paper, least staining power ranked first)

- #5 1st
- A 2nd
- #3 3rd
- B 4th
- #2 5th
- #1 6th
- #4 6th

*Evaporation:* (on white paper, shortest time ranked first)

- #5 1st
- A 2nd
- #2 2nd
- B 4th
- #3 4th
- #1 4th
- #4 7th

*Odor:*

- #5 and A-equal
- #1-2-4 and B-equal
- #3-objectionable odor and color.

“When used for varnish reducing, and carefully watched, we were unable to note any perceptible difference, either in setting or in completed drying after 24 hours. What we considered the most delicate test in practical use was in using them for thinning quick drying black, and the results here were as follows (the time given is in minutes and represents the time when the black had dried sufficiently hard to be varnished over without rubbing up)

- |          |             |
|----------|-------------|
| A        | 50 minutes  |
| B-1-2-5  | 90 minutes  |
| #3 and 4 | 105 minutes |

“After six days the quick drying black which had been thinned with these various turpentines was examined, and we found that a sample thinned with A showed little or no tendency to thicken up; #5 thickened slightly; and the balance had all thickened quite a little but showed practically no differences.

"In a general way I would say that it is our judgment that for the general purposes for which material of this kind is used, odor is the most important feature, inasmuch as unfortunate odor has been the greatest objection to a large use of this class of material in the past, and at the present time it is the main cause of the prejudice against it.

"From the standpoint of working qualities there is as you will note quite a decided action in slowing up the drying. I am not aware as to just what causes this, and of course for many purposes it would not be serious. There are many uses however for quick drying color where the time requirements are so imperative that none of these materials could be used. We do not understand why the same measure of influence on the drying does not show up in connection with varnishes, but as a matter of fact it does not.

"We should say that your sample #5 is decidedly better in general characteristics than any wood turpentine we have ever seen. In every point excepting the drying in quick drying black it shows up entirely equal to straight turpentine.

"#1-2-4 are satisfactory as wood turpentines, and would be usable for all purposes for which high grade wood turpentine is at the present time usable.

"The sample tested under "B" represents wood turpentine of which we have used a considerable quantity, and with which we have had practically no trouble excepting from the standpoint of odor.

"It is impossible at the present time to substitute wood turpentine for a pure spirits, in many places, on account of the stronger odor, and from this standpoint your sample #5 looks particularly interesting."<sup>1</sup>

<sup>1</sup> The large variation in the drying properties found by the quick drying black test indicated that this test offered a fairly simple method of determining the effect of the removal of the heavy oils on the drying properties. Small samples of each of the five turpentines were redistilled so as to prepare samples containing no heavy oils and these special samples were submitted for the drying test. It was reported that the time of drying of all the samples had been brought closer together and closer to that of gum turpentine.

## REPORT II

"Sample was taken from each can and compared in laboratory with pure gum spirits. The only objection raised being the decidedly objectionable odor in the #3 as well as the objectionable odor and slow evaporating in #5.

"The samples were then tested as a thinner or solvent in an ordinary House Paint and the same results obtained, the man applying the goods objected to the odor of both #3 and #5.

"I then melted a batch of varnish and divided it into six equal parts thinning five of these with the five samples of Wood Turpentine and the sixth part with pure gum spirits<sup>1</sup> so that the body or base of all are identical.

"After filtering and settling these six varnishes were submitted to practical tests by our head tester who reports as follows:

|                     |   |
|---------------------|---|
| Working with Brush, | Good.   |
| Drying              | { #3 and #6 best.<br>#1, #2, and #4 fair.<br>#5 slow. |

"Color all up to standard, odor #3 and #5 strong odor, #3 most objectionable, #1, #2, and #4 fair, #6 sweet.

"In having this test made we took great care both in making and testing the varnish. The man who tested did not know that he was not testing a regular run of six batches of one of our standard varnishes which shows conclusively that he was doing his duty in an unbiassed manner and as you will note his report on odor corresponds with both laboratory report and test made by painter."

## REPORT III

"Material or Subject—Wood Turpentine Nos. 2, 3, 4, and 5. From—United States Dept. of Agriculture—Forest Products Lab.

Remarks—For a comparative test with Pure Gum Turpentine as to suitability for varnish making.

<sup>1</sup> Reported as No. 6.

| <i>I. Chemical Tests</i>  |              |                          |                 |                              |             |
|---------------------------|--------------|--------------------------|-----------------|------------------------------|-------------|
|                           | #2           | #3                       | #4              | #5                           | Gum Turps.  |
| Specific Gravity...       | 0.864        | 0.868                    | 0.870           | 0.866                        | 0.865       |
| Residue on Evap...        | 0.64%        | 2.60%                    | 0.79%           | 0.67%                        | about 0.60% |
| Iodine Absorption..       | 371.6%       | 298.7%                   | 388.5%          | 392.9%                       | 429%        |
| <i>Distillation Test:</i> |              |                          |                 |                              |             |
| Boiling Point.....        | 154°C        | 155°C                    | 150°C           | 153°C                        | 154°C       |
| -165°C.....               | 86%          | 40%                      | 87%             | 91%                          | 95%         |
| 165°-175°C.....           | 9%           | 44%                      | 8%              | 6%                           | 5%          |
| Over 175°C.....           | 5%           | 16%                      | 5%              | 3%                           | ....        |
|                           | 100%         | 100%                     | 100%            | 100%                         | 100%        |
| Color.....                | W. W.        | Pale<br>Straw            | W. W.           | Very<br>pale<br>Straw        |             |
| Odor.....                 | Best<br>Mild | Rank<br>Penetra-<br>ting | Third<br>Greasy | Second<br>Good but<br>strong |             |

II. Varnish-making tests: Solvent power was tested by mixing 10 parts of each sample (also of Gum Turps.) with 1 part of a hard gum varnish. The pure turpentine precipitated the gum within  $\frac{1}{2}$  hour: #2 followed very shortly, then #5 (after about 6 hours). #4 held the varnish in solution, showing only a slight separation at the surface-edges after a week: #3 held the varnish in solution perfectly for more than two months.

"Other qualities were tested by reducing equal weights of the gum and oil from an agricultural varnish taken from the same batch, with equal volumes of the samples as well as with pure turpentine, in such a way as to have all conditions as nearly as possible the same. The varnishes so made were not filtered, but were allowed to settle and age for three months. The percentage of volatile matter was then determined and the varnish was submitted to the usual tests of body, flowing, drying, brushing, etc.

"The percentages of volatile matter were: For (I) varnish made with Gum Turps., 53.50; (II) #2 54.87; (III) #3 52.35; (IV) #4 53.32; (V) #5 54.10. The gum turp. varnish was the same in "body" as IV (as shown by the rate of rise of the air bubble in a



narrow test tube of the varnish); II and V were both slightly lighter in body, as would be expected from the higher percentage of volatile matter; but on the other hand III was still thinner, tho showing less volatile. This fact is doubtless due to the much greater solvent power of Turpentine #3, which results in a much less viscous solution.

"Varnish IV showed the poorest flowing qualities; V was slightly better, I and II (in order) still better, and III much the best. The drying test shows that the varnishes with lighter body dry faster and harder, tho II in drying faster than III, shows an exception. The relative order is II first, III, V, IV, I. From a consideration of factors involved, it is evident that if all were brought to the same body, II, V, and IV would dry at about the same rate, followed by III and I.

"In brushing qualities Varnish I was ranked first, V next, III next, followed by IV and II. This ranking denotes the comparative ease with which a smooth, glossy film of proper thickness can be obtained upon a filled board.

"The results of the tests may then be summarized as follows:

"The samples are all stronger solvents than Gum Turpentine, #3 being the strongest, #2 and #5 only slightly better than the Gum Spirits. If odor could be disregarded, #3 would probably be in all respects the best substitute for Gum Spirits and would be an improvement on it in some ways; but #3 is too disagreeable in smell to be used, except in small proportions. The choice therefore lies between #2 and #5, with the majority of points in favor of the latter."

## REPORT IV

### PAINT MANUFACTURERS' ASSOCIATION

*"Varnish Tests Made with Wood Turpentine Submitted by U. S. Forest Products Laboratory"*

"Two grades of varnish were made up from each of the wood turpentine—rubbing varnish, and spar varnish. The formulas used throughout in making up these varnishes are as follows:

| RUBBING VARNISH |                  | SPAR VARNISH    |                 |
|-----------------|------------------|-----------------|-----------------|
| By measure      | By weight        | By measure      | By weight       |
| Gums.... 21.4   | Gums .... 27.97  | Gums .... 16.4  | Gums .... 20.17 |
| Oils ..... 19.4 | Oils ..... 18.62 | Oils ..... 42.3 | Oils ..... 41.5 |
| Turps.... 59.2  | Turps .... 53.26 | Turpentine 41.3 | Turpentine 38.2 |
| —               | Driers .... .15  | —               | Driers .... .13 |
| Total ..100.0   | —                | Total ...100.0  | —               |
|                 | Total 100.00     |                 | Total 100.00    |

"In the manufacture of the varnishes it was noted that Nos. 2 and 4 had the best odor, while Nos. 1, 3, and 5 under heat gave off strong odors, somewhat irritating to the eyes. By heating up the various turpentines alone to 100° and observing the odor, the same result was obtained.

"The varnishes which were manufactured from these turpentines were applied to oak panels six inches wide, twelve inches high, and one inch thick. After the panels had been properly coated, they were subjected to a series of tests, and the data obtained from these tests is also recorded in the charts on the following pages.

#### *"Paint Tests with Wood Turpentines"*

"After the varnish test had been finished, the various turpentines were used to thin one standard paint formula, and this paint formula was applied to a series of panels to be placed on the Southern Test Fence. The formula selected for the test consisted of 45 parts corroded white lead, 45 parts zinc oxide, 5 parts of asbestine, and 5 parts of whiting. This paint was divided into portions and thinned respectively with the five turpentines submitted for test. The paint formula itself was made up in condition resembling a ready mixed paint, as found upon the market, but containing nothing in the vehicle portion except linseed oil and drier. This formula was thinned in the proportion of one pint of turpentine to a gallon of paint for the priming coat, and  $\frac{1}{2}$  pint turpentine and  $\frac{1}{2}$  gallon linseed oil for the second coat. The third coat was used without reduction. During the application of these paints the painter noted that No. 3 had a very objectionable odor, while Nos. 1, 2 and 4 had a very good odor, No. 2 probably being the best. In working and flattening

## EXTERIOR VARNISH

| No.<br>Panel No.<br>No. of Coats<br>Odor                                   | 1<br>I  |  | 2<br>II   |   | 3<br>III  |   | 4<br>IV   |   | 5<br>V   |  |
|--|---|--|---|---|---|---|---|---|--|--|
|  | Three   | Three  | Three   | Three   | Three   | Three   | Three   | Three   | Three  | Three  |
| Action on c's  | Fair; resembles gum turpentine but not quite as nutty               | Excellent odor; as good as pure gum turpentine       | Extremely bad odor. Resembles pyroligneous acid and acetone | Fair; resembles turpentine                          | Extremely irritating                                | Fair; resembles turpentine                          | Fair; resembles turpentine                          | Fair  | Fair   | Fair   |
| Ease of Application  | Slight ethereal odor  | None   | None  | Extremely irritating                                | Extremely irritating                                | Extremely irritating                                | Extremely irritating                                | None  | None   | None   |
| General Working Character  | Easy  | Easy   | Drys quickly  | Easy  | Easy  | Easy  | Easy  | Very slight   | Easy   | Easy   |
| Color Density <sup>1</sup>   | Good  | Good   | Pulls when dry  | Good  | Easier than I or II                                 | Good  | Good  | Good  | Good   | Good   |
| Period of Tackiness  | A<br>A coat—3 hr. 30 min.<br>B " 6 hr. 10 min.<br>C " 6 hr. 60 min. | B<br>3 hr. 30 min.<br>6 hr. 10 min.<br>5 hr. 45 min. | D<br>2 hr. 50 min.<br>6 hr. 5 min.<br>5 hr. 35 min.         | D<br>2 hr. 50 min.<br>6 hr. 5 min.<br>5 hr. 35 min. | D<br>2 hr. 50 min.<br>6 hr. 5 min.<br>5 hr. 35 min. | D<br>2 hr. 50 min.<br>6 hr. 5 min.<br>5 hr. 35 min. | D<br>2 hr. 50 min.<br>6 hr. 5 min.<br>5 hr. 35 min. | D<br>2 hr. 50 min.<br>6 hr. 5 min.<br>5 hr. 35 min. | C<br>2 hr. 55 min.<br>5 hr. 30 min.<br>5 hr. 15 min. | C<br>2 hr. 55 min.<br>5 hr. 30 min.<br>5 hr. 15 min. |
| Period of Hard Drying  | Allowed 2 days between application of first and second coats        | 4 days allowed between second and third coats        | 11 seconds<br>(Average of 3 trials)                         | 11 seconds<br>(4 trials)                            | 7.6 seconds<br>(3 trials)                           | 10.7 seconds<br>(7 trials)                          | 10.7 seconds<br>(7 trials)                          | 11 seconds<br>(4 trials)                            | 11 seconds<br>(4 trials)                             | 11 seconds<br>(4 trials)                             |
| Body (Rise of a bubble 2.5 cm. long in a tube .8 cm. dia. and 28 cm. long) | 10 seconds<br>(Average of 3 trials)                                 | 11 seconds<br>(4 trials)                             | 11 seconds<br>(4 trials)                                    | 11 seconds<br>(4 trials)                            | 7.6 seconds<br>(3 trials)                           | 10.7 seconds<br>(7 trials)                          | 10.7 seconds<br>(7 trials)                          | 11 seconds<br>(4 trials)                            | 11 seconds<br>(4 trials)                             | 11 seconds<br>(4 trials)                             |

<sup>1</sup>A, B, C, and D indicate degrees of darkness. A being darkest and D lightest.

## RUBBING VARNISH

| No.<br>Panel No.<br>No. of Coats<br>Odor                                 | 1<br>VI   |   | 2<br>VII   |  | 3<br>VIII                                       |   | 4<br>IX   |                           | 5<br>X  |      |
|--|---|---|--|--|---|---|---|---------------------------|---|------|
|  | Three   | Fair; resembles gum turpentine but not quite as nutty | Three  | Excellent odor; as good as pure gum turpentine | Three   | Extremely bad odor. Resembles pyroligneous acid and acetone | Three   | Fair resembles turpentine | Three   | Fair |
| Action on Eyes   | None  | Slight ethereal odor                                  | None   | None   | Extremely irritating                            |   | Very slight                                     |                           | None  |      |
| Ease of Application  | Easy  |   | Works easily at first but dries quickly and pulls on rubbing |  | Very easy. Does not dry readily under brush     |   | Harder to rub than VIII but easier than VII     |                           | Same as No. 2                                   |      |
| General Working Character  | Good  |   | Good   |  | Good  |   | Good  |                           | Good  |      |
| Color Density <sup>1</sup>   | A   |   | C  |  | D   |   | A   |                           | B   |      |
| Period of Tackiness  | A coat—1 hr. 35 min.<br>B " 1 hr. 30 min.<br>C " 2 hr. 30 min.                          |   | 1 hr. 35 min.<br>1 hr. 25 min.<br>2 hr. 25 min.              |  | 1 hr. 20 min.<br>1 hr. 25 min.<br>2 hr. 20 min. |   | 1 hr. 30 min.<br>1 hr. 30 min.<br>2 hr. 15 min. |                           | 1 hr. 20 min.<br>1 hr. 30 min.<br>2 hr. 10 min. |      |
| Period of Hard Drying  | Allowed 2 days before applying second coat<br>Allowed 4 days before applying third coat |   |  |  |   |   |   |                           |   |      |
| Body (Bubble 2.5 cm. long rises in tube .8 cm. diameter and 28 cm. long) | 8 seconds<br>(5 trials)   |   | 9.8 seconds<br>(5 trials)                                    |  | 6.7 seconds<br>(5 trials)                       |   | 9.8 seconds<br>(7 trials)                       |                           | 9.0 seconds<br>(6 trials)                       |      |

Temperature of laboratory during application of varnish A coat, 90.5° F. B coat, 93.2° F. C coat, 86° F.  
<sup>1</sup>A, B, C, and D indicate degrees of darkness, A being darkest and D lightest.

properties, Nos. 1, 2, 4 and 5 gave the best results, and fully as good results as with the use of pure gum spirits. . . .

"The evaporative values of these turpentines are satisfactory in every case, No. 3 evaporating more rapidly than the others, and none of them leaving any stain."

NOTE:—The panels painted with these test paints were exposed in September, 1910 (see Bulletin 30, Paint Manufacturers' Association), and the report of an inspection made in Feb., 1912, includes the following paragraph:

"The panels which were painted with pigment Formula 31 ground in pure linseed oil and reduced with various wood turpentines as thinners, indicated that the highest types of these materials were well suited to replace pure gum spirits of turpentine as a thinner for paints to be exposed out-of-doors. Wood Turpentine No. 2 gave the whitest surface, while Wood Turpentine No. 5 gave the darkest."

## REPORT V

"#2, this is the best sample both in regard to odor and color and other qualities; it compares satisfactorily with Gum Spirits.

"#4 and #5, these rank about the same from our point of view, being somewhat inferior to #2. #4 is lighter in color but #5 has less objectionable odor.

"#1, this is next in quality to #4 and #5.

"#3, this is the least desirable of the lot, having very disagreeable odor and very dark in color. It also forms considerable residue when distilled with steam.

"From a commercial point of view, we believe that #2 could be used to a considerable extent in the Paint and Varnish Industries in place of Gum Spirits, but the odor of all the others would prevent their use except in a very small way."



## THE PAST, PRESENT, AND FUTURE OF THE NAVAL STORES INDUSTRY

BY CHAS. H. HERTY

*University of North Carolina, Chapel Hill, North Carolina*

The limited use of the oleoresinous exudate of pine trees dates back many centuries, but the real beginning of an industry on a large scale is closely associated with the discovery of the vast pine forests which extend along the southeastern and southern coasts of the United States from North Carolina to Texas.

These forests lie chiefly in the coastal plain and in the slightly hilly country between the Piedmont plateau and the coastal plain, a strip varying in width from one hundred to two hundred miles and characterized by a sandy soil, covered for the most part with "wire grass," this furnishing a beautiful carpet of green in spring and summer, but making a serious fire risk in winter. The longleaf pine readily sheds its lower limbs, especially in close stands, so that the forests are remarkably open and free from that undergrowth, which, in the northwest, leads to such destructive forest fires.

The early settlers in eastern North Carolina began the exploitation of their forests of longleaf pine for the purpose of providing tar and pitch for use in the construction of wooden ships, and gradually extended their operations to the collection of crude turpentine which was shipped to northern cities or England for distillation. The forests covered the entire territory and, as clearings for farms were needed, destructive methods of operation were welcomed and encouraged.

At the same time limited operations were being conducted upon the maritime pine in southwestern France between Bordeaux and Bayonne. To receive the crude turpentine the French made use of a hole dug in the sand at the base of the tree. The oleoresin flowing from the wound on the trunk above was col-

lected in these holes. Necessarily by this method much of the material was wasted and rendered impure.

#### AMERICAN METHOD OF COLLECTION

In North Carolina the method of collection was improved, or thought to be improved, by cutting a large opening, the "box," in the base of the tree. Into this box the crude turpentine flowed and was collected at regular intervals. The conservative character of the men engaged in this industry led to the continuance of this wasteful and destructive method of "boxing" until the very recent past.

Briefly, the method of operating so long in use in the United States is as follows: In the winter the laborers are engaged in cutting "boxes." Each box is then "cornered," a wide chip being removed from each half of the box to provide a surface suitable for directing the flow of crude turpentine to the box. Meanwhile, other laborers are employed in clearing all combustible material from around each tree, "raking." Ground fires are then started to consume the dead wire grass, chips, etc. With the opening of Spring "chipping" begins. This consists in scarifying each week the trunk of the tree above the "cornered" surface by means of a "hack," a U shaped steel tool set in a wooden handle. Attached to this handle is a heavy iron weight to give momentum to the free arm swing used in chipping. After four or five weeks the "boxes" average a good filling and the crude turpentine, "dip," is then transferred to buckets by flat, iron paddles, and from the buckets it is collected in barrels conveniently placed in the woods. In the Fall, at the end of the chipping season, the hardened oleoresin, which has gradually collected during the chipping season on the scarified surface of the tree, is removed by scraping, giving thus the name "scrape" to this product, which is sold as "Gum Thus," or distilled. In the following Winter the trees are again raked and the grass fired, and in the Spring chipping is resumed at the point on the trunk of each tree where it ceased the previous year. This cycle is usually continued from three to four years, although in early days it was often continued ten or twelve years, the scarified surface extending high on the trunks. Necessarily

the yield from such high chipping was largely decreased, owing to the increased distance of flow to the receptacle.

In the early days of the North Carolina industry, no effort was made to distill the product, but gradually it became clear that it would be better to separate the crude turpentine into spirits of turpentine and rosin by distillation in the woods. For this purpose iron stills were used at first, but results were unsatisfactory until the introduction of copper stills, which were less liable to crack and could be heated with greater uniformity and better control.

The industry now began to grow rapidly and before many years it was found that the supply of available timber in North Carolina was rapidly decreasing. This led many of the operators to transfer their operations to the virgin forests of the adjoining state, South Carolina, where the same destructive methods were applied by the same men or their descendants. In this way, and for these reasons, the center of the industry has gradually moved southward and then westward as evidenced by the relative prominence of the ports for exports of the products; first Wilmington, N.C., then Charleston, S.C., then Savannah, Ga., and now the latter, together with Jacksonville, Fla., and the gulf ports, Tampa, Fla., Pensacola, Fla., Mobile, Ala., Gulfport, Miss., New Orleans, La., and others.

#### FRENCH IMPROVEMENTS

The steady growth of the American industry received a serious check during the Civil War. The consequent scarcity of the products was accompanied by an abnormal increase in their value. This enhanced valuation led Hugues, a Frenchman, to propose a less wasteful method for the French forests than the hole dug in the sand. He proposed as a substitute a clay pot, holding about one pint. This pot was supported on its bottom by a large nail driven into the tree and on one side of its upper rim by a strip of sheet zinc, approximately 2" x 4", slightly curved and driven into a corresponding upwardly inclined cut in the wood. This spout served to direct the oleoresin into the pot. At first his proposition was scoffed at and the peasants amused themselves by breaking the little pots. It is a pitiful

commentary that Hugues died in poverty; but his ideas lived and gradually became adopted in France.

#### AMERICAN IMPROVEMENTS

As the knowledge of the new method in France spread to this country, numerous efforts were made to apply similar forms of apparatus to the American system of chipping, but for many years such efforts failed. No less than fifteen patents were issued in the United States on this subject, but no one of them proved a commercial success.

Eleven years ago the writer began a series of field experiments on a small scale in the turpentine forests of South Georgia. One feature of these experiments was the use of a modification of the Hugues system, consisting of two separate metallic gutters, inserted in upwardly inclined cuts in the tree, along which the oleoresin flows. The upper and shorter gutter is separated at its lower end about one inch from the lower gutter and empties into it. The lower gutter extends from two to three inches beyond the center of the angular scarified surface formed in chipping, and serves as a spout to convey the oleoresin to a cup suspended from a nail just below the end of the gutter. These cups are made of either well burned clay or galvanized iron, and have a capacity of one quart.

Attracted by the promising character of these preliminary experiments, the U. S. Bureau of Forestry began a series of field tests of the apparatus on a large scale, the work being under the immediate supervision of the writer. Before the end of the first season of testing it was evident that the apparatus was a practical success, and the results attained, both as to quantity and quality of oleoresin, justified the hope of immediate commercial introduction of the system. But the habits of long years made difficult the adoption of such an innovation. This ultra-conservatism was slowly overcome and the adoption of the new system spread rapidly. Only a few years more will be required to witness the complete replacement of the "box" by the "cup" system in American forests. A detailed account of these experiments is given in Bulletin No. 40 and Circular No. 34 of the U. S. Bureau of Forestry.



With the main points at issue settled, namely—improved yields both in quantity and quality of the products and preservation of the trees, other forms of apparatus were devised to meet the objections of some of the operators to certain points in the cup and gutter system. Many of these have never proved practical, but some have been introduced on a considerable commercial scale.

The successful outcome of the experiments on the relative yields from the "box" and the "cup" system led the United States Forest Service to further experiments in more conservative treatment of the trees in chipping. Comparative studies were made of the yield from deep and shallow chipping and the latter found to give the greater yield during a period of four years of operation. Other experiments showed that a less rapid rate of ascent of the trunk also gave larger yields, and experiments combining these several modifications of present practices showed a largely increased yield. A final set of experiments pointed clearly the rational way to a perpetuation of the naval stores industry in America. The details of this investigation are given in Bulletin No. 90 of the United States Forest Service.

#### DISTILLATION

In the matter of distillation, only slight advances have been made in America. The uniform process consists in the use of a large copper kettle and condensing worm. The charge for a distillation averages nine to ten barrels of crude turpentine. The kettle is heated by free flame and during the distillation a small stream of hot water from the top of the condenser tub is admitted through an opening in the upper part of the kettle, thus facilitating the removal of the volatile oil. The condensed spirits of turpentine and water separate in the receiver, owing to difference in specific gravity, and the lighter spirits of turpentine is transferred to oak barrels, well coated with glue on the inside. No effort is made to redistill this product, and it always comes upon the market contaminated by a small amount of resin carried over mechanically during distillation. After most of the volatile oil has passed off, the still cap is removed, excess water in the kettle boiled off, and the molten rosin drawn off



through a tap in the bottom of the kettle onto a coarse wire filter, then through a second filter of fine mesh wire overlaid with cotton batting. The molten rosin is then dipped into wooden barrels luted with clay and solidifies on cooling. In this condition it is shipped to market.

The usual method of controlling the distillation is by the sound heard at the mouth of the condenser worm. Within the past three years a number of American operators have substituted for this method that of thermometer control with very excellent results.

In France, much more progress has been made in the art of distillation. Among the French distilleries there are three distinct types: first—a system closely resembling the American; second—distillation solely by steam in steam jacketed vessels; and third—a mixed system in which there is direct contact of fire with the kettle during the first stage of the distillation, then replacement of this by mixed injection of steam and hot water. By this means, a constant temperature is maintained, enabling the complete removal of all spirits of turpentine without danger of scorching the rosin.

It can readily be understood that in France, under proper methods of forestry, with conservative tapping of the trees and provision for systematic reforestation, a distillery can look forward to a permanent supply of raw material. Hence there is justification for the more costly plants and more efficient methods of distillation; but in America, where under past methods the industry shifts so rapidly so great an outlay of capital for this purpose would not be justified. There is no doubt that with an excellent "stiller" very good results can be obtained under the American system, but the personal element of the stiller enters into the question and this could be easily avoided without any great outlay of capital by adopting the French system of mixed injection.

Quite recently M. Castets has erected near Dax, France, a distillery which combines the features of continuous distillation in a partial vacuum and condensation by pressure of the waste spirits of turpentine vapors from the ordinary condenser in a

second condenser attached to the first, thus increasing notably the yield of volatile oil and improving the quality of the rosin.

#### THE INDUSTRY IN OTHER COUNTRIES

There is no need of any especial consideration of the Spanish industry which has developed considerably during the past decade. The operations are essentially the same as the French, and the same species of pine, *pinus maritima*, is exploited.

In Austria the industry is more limited and is even more destructive than by the old American system; a "box" being cut in the base of the tree, *Pinus Laricio*, and the trunk of the tree scarified for at least fifty per cent of its circumference, the oleoresin being directed towards the center of the scarified surface by thin wooden strips inserted in downward cuts in the tree.

In Russia the chief tree exploited is *Pinus Sylvestris*. Climatic conditions do not admit of the usual process of collecting the crude turpentine at regular intervals. Instead, the trees are scarified in Spring over a space about three feet high and almost encircling the tree. During the year a mass of hardened rosin collects on this surface. In the Winter it is scraped from the tree and distilled for its volatile oil and resin. This process is repeated for five years. The tree is then felled and the resinous portion of the tree subjected to destructive distillation. In other districts no effort is made to collect the rosin from the trees annually, but this is allowed to remain until the end of the fifth year of scarification. The tree is then felled and that part containing the rosin distilled first at a low temperature to obtain the volatile oil, then at a more elevated temperature to obtain tar and charcoal by destructive distillation of the wood.

The spirits of turpentine from Germany, Sweden, and Finland, seems to be a product solely of the destructive distillation of resinous wood.

The production of naval stores in India and other tropical countries is at present on too small a commercial scale to call for any detailed discussion here.

## WOOD SPIRITS OF TURPENTINE

Among the various departments of the naval stores industry in America none has had a more varied and interesting career than that of the production of "wood spirits of turpentine" by destructive distillation of resinous wood. Years ago considerable capital was invested in plants for utilizing the by-products formed during the destructive distillation of "fat lightwood." None of the plants were commercially successful and for awhile nothing was heard of the industry. But with the increase in price of spirits of turpentine resulting from the formation of the Turpentine Operators Association in 1902 a fresh impetus was given to the "wood spirits of turpentine" industry. At first somewhat crude methods of destructive distillation were advocated, and as the promoters of this industry appealed largely to local interest in having stumps for distillation removed from fields suitable for cultivation, a double impetus was received. Much enthusiasm was aroused, and a number of plants constructed. But the industry received a serious blow in the refusal of the varnish makers to use the impure "wood spirits of turpentine" manufactured, by the failure to find a market for many of the heavier oils and the coke, and by the destruction by fire of many of the improperly constructed plants.

The price of spirits of turpentine continued to rise and led to the development of the steam extraction process for manufacture of wood spirits of turpentine. After thorough grinding, the wood is treated in iron retorts with steam, and the volatile oil distilled, no effort being made to obtain any other product. By one redistillation of the product a very high grade spirits of turpentine is obtained, equal, if not superior, to that from the living tree. Unfortunately, the yield is not sufficiently large to make the process remunerative.

Quite a different process is employed by those plants which utilize a bath of molten rosin for removal of the spirits of turpentine from the wood, with subsequent distillation of the volatile oil from this bath. Such plants seem to have met with a fair measure of success.

More recently, extraction processes have been developed

which employ low boiling petroleum products as the extractive. Such plants recover both the spirits of turpentine and the rosin from the ground wood, and have a great advantage in the present very high value of rosin. These plants are also utilizing the refuse from the straining of rosin at the distilleries in the woods, a product formerly burned on the waste piles, but now bringing nineteen dollars per ton. This method is adding a considerable amount to the annual output of rosin.

The most recent development is a plant for destructive distillation of wood in retorts heated by jackets filled with high boiling petroleum fractions. By this means the fire risk is practically completely eliminated and the results indicate that by means of the complete and ready temperature control of the oil jacket larger yields of better products can be obtained.

#### ANNUAL PRODUCTION OF NAVAL STORES

No subject connected with the naval stores industry admits of so little accuracy of statement as does that of statistics on the total annual production. The most careful estimates are at best only approximations. This is unfortunate, for in the past it has frequently led to speculative manipulations of the market and the temporary establishment of values which had no legitimate basis depending on supply and demand.

The following table of annual production is given therefore, as an approximation only, but it is believed to be a reasonably accurate approximation:

|                                | Spirits of Turpentine<br>(barrels 52 gallons) | Rosin<br>(barrels 500 lbs.) |
|--------------------------------|---|-----------------------------|
| America.....                   | 600,000                                       | 2,100,000                   |
| France.....                    | 100,000                                       | 350,000                     |
| Spain.....                     | 25,000  | 87,500                      |
| Austria.....                   | 3,000   | 10,500                      |
| Other countries.....           | 50,000 (?)                                    | (?)                         |
| Total estimated production.... | 778,000                                       | 2,548,000                   |



### PRODUCTION OF CRUDE TURPENTINE PER TREE

Here again definite figures are difficult to give; for there is no reliable information concerning the number of trees in operation. Furthermore, there is often very wide variation in the producing power of adjacent trees of the same species, size, and crown. But from the data in the publications of the United States Forest Service, an average American pine, worked under the cup system, will produce, during four years of operation, an annual average of ten pounds of crude turpentine and two and a half pounds of "scrape," the proportionate yield being considerably greater during the first and second than during the third and fourth years of operation.

The average daily flow of crude turpentine during one week from a freshly chipped surface on such pines is shown in the following table, the results having been obtained during the summer of 1901 on trees near Statesboro, Georgia:

| Day   | Yield per tree (grams) |      |       | Average yield<br>(grams) | Per cent<br>average yield |
|-------|------------------------|------|-------|--------------------------|---------------------------|
|       | 1                      | 2    | 3     |                          |                           |
| 1     | 113.0                  | 46.5 | 89.0  | 82.8                     | 62.9                      |
| 2     | 22.5                   | 7.5  | 16.0  | 15.3                     | 11.6                      |
| 3     | 13.5                   | 6.5  | 16.0  | 12.0                     | 9.1                       |
| 4     | 9.0                    | 5.0  | 17.0  | 7.0                      | 5.3                       |
| 5 & 6 | 9.0                    | 5.0  | 23.0  | 12.3                     | 9.3                       |
| 7     | 1.0                    | 2.0  | 4.0   | 2.3                      | 1.8                       |
| Total | 168.0                  | 72.5 | 165.0 | 131.7                    | 100.0                     |

### TSCHIRCH'S VIEWS ON RESIN FLOW

As to the seat of resin production and cause of resin flow, most valuable and important views have been advanced by Prof. A. Tschirch in his book "*Die Harze und die Harzbehälter*," 2nd edition. Tschirch has shown that the seat of resin production is a mucilaginous layer lining the inner walls of the resin ducts. These ducts he divides into two classes: First—primary



ducts, whose resin is to be considered a true physiological product. Such ducts occur irregularly and in varying number in any pine. They play only an insignificant role as producers of commercial crude turpentine. Second—secondary resin ducts which form in large numbers in the outer layers of the new wood after a tree is wounded, both above and below the wound. Their oleoresinous exudate is, therefore, a pathological product. It is from such pathological ducts that the great bulk of crude turpentine is obtained.

The application of these views to practical problems in the turpentine forests has already yielded important and fruitful results.

#### FUTURE OF THE INDUSTRY

During the past few years the statement has frequently been made that from present indications the naval stores industry must cease to exist, at least as a large industry, within the next twenty years. While it is true that there are danger signals which must be heeded, such pessimistic views do not seem to be well grounded.

Certainly in France and consequently in Spain, where the same system is in operation, the industry has been placed upon a self-perpetuating basis.

In America we have been prodigal with our wealth of virgin forest.

But it must be remembered that until the last decade these forests have had a very low commercial valuation. The average price for well timbered lands in our southern states not many years ago was approximately one dollar per acre, land, timber, and all. Indeed, the popular term applied to all holders of large tracts of such lands was "land poor," as expense of taxation, protection, etc., exceeded any hope of probable profit. This condition was largely due to lack of transportation facilities, insecurity of title, low price of naval stores and lumber, lack of knowledge of the farming value of much of the land on which these forests stood, and the belief that the forests were inexhaustible.

Now conditions have entirely changed. Railroads penetrate

every portion of the territory, titles have been cleared, prices of naval stores have brought wealth to the operators, the lumbermen from Michigan, Wisconsin, and other northern states have turned from the rapidly disappearing white pine forests of the north to those of the southern yellow pine; where forests once stood farms have been developed which surpass in fertility any other portion of the southern states, and a clear knowledge has been gained that the forests are by no means inexhaustible. Furthermore, the spirit of conservation of natural resources has made itself felt in this field as well as in those of minerals, water power, etc.

The consequence of these changes has been a very rapid enhancement in the value of such holdings. And with increased valuation comes naturally the desire to protect and use conservatively. Unquestionably the stand of virgin forest will still further diminish, for the demand for farm lands is active, the call for lumber imperative, and the danger of tropical storms along the Gulf Coast ever present. With such diminution in supply will come still further enhancement in values and still more conservative methods of operation.

So much for the present stand of virgin forest. If the situation were limited to this alone, the outlook might be considered gloomy. But it must be remembered that there are vast tracts of cut-over lands in portions of the southern states whose clay sub-soil lies so deep that the lands are not suited to agriculture. On such lands the longleaf pine, with its long tap root, prospers. Magnificent forests once covered every acre of such lands and fortunately tree planting is not required to reproduce such forests. Nature alone will again cover this territory with a wealth of forest, provided Nature is given an opportunity; for the most superficial observer who travels through this territory will testify that where conditions have been favorable natural reproduction has brought again splendid, though small, young forests.

Against this willingness of Nature to restore this rich heritage to us, stand three agencies:

First, and of least importance, the consumption by hogs of the delicately flavored and nutritious seed of the longleaf pine.

This is a real factor in certain somewhat restricted districts. The constantly spreading sentiment for "stock laws" will check this evil.

Second, and of the very greatest importance, the destructive action of the ground fires, Fig. 7, which annually sweep over the entire turpentine belt. Such fires destroy the myriads of young seedlings which can readily be seen springing up in the wire grass which surrounds them on every side. The seedling devotes the greater part of its early energies to sending down its long tap root through the deep sands rather than to strengthening its stalk above ground; hence, in most cases, it is not able to withstand the constantly recurring ground fires. The doctrinaire may rail against the evils of such firing of the woods, but from one who has lived among the turpentine camps there comes no word of reproach against the turpentine operator who "burns the woods." His all is invested on the outer surface of his trees. A serious outbreak of fire during midseason means financial ruin. The carelessness and sometimes viciousness of laborers is too serious a risk to run with a mass of dead wire grass covering every foot of his territory. Naturally he protects himself by burning this grass when he is prepared for it, after "raking season."

Where then is the hope for reforestation? In the realization of the value of the waste cut-over lands where turpentine operations cannot be carried on for lack of timber. Such lands have now but little value, but the lesson of France shows that even there a reasonable income begins from artificial reproduction within a period of twenty years and then rapidly increases. With our warm southern climate the prospect for rich returns from such investments should be even greater than in France.

Third, the greed of man. If we are to have a self-perpetuating industry, even stock laws and the reforestation of waste lands will not avail if a practice on the part of turpentine operators during the past two years continues. The abnormally high price of spirits of turpentine two years ago led to a wild scramble for timber for increased operations. At the same time the efficiency of the cup system was just gaining wide recognition. Realizing that a tree too small to have a "box" cut in it could

be worked with a cup hung upon it, the operators throughout the whole region proceeded to cup every small tree to which access could be gained. In many cases new farms were opened on old abandoned territory where natural reproduction had furnished thrifty young forests. The result was over-production of crude turpentine. The temporary benefit to the consumers in the drop in values following this over-production was dearly bought, for the price was the destruction of young forests which in time should have produced their full share of the world's need of spirits of turpentine and rosin. Common sense must and will govern in this matter. It is only necessary for the operators to realize that the yield from such saplings does not meet the cost of production, then the practice will cease.

Surely the above considerations justify an optimistic view of the future of the naval stores industry. But experiment, demonstration, statistics, and knowledge of progress made in other lands, must lead the way for the man in the woods.

## SHELLAC ANALYSIS AND THE DETECTION OF SMALL AMOUNTS OF COLOPHONY IN SHELLAC

BY EDWIN F. HICKS

*Philadelphia, Pa.*

The adulteration of shellac with colophony or common rosin has been extensively practised in recent years, though during the past two or three years it has not been so conspicuous and flagrant as formerly; doubtless owing chiefly to the relatively lower prices which have prevailed in the shellac market for the pure grades during this period.

While the best marks, bearing certificates, can, as far as the writer has observed, be accepted as free from sophistication, many of the intermediate grades are liable to contain added rosin in variable amounts, and the cheaper grades, especially some varieties of button-lac, are still subject to flagrant adulteration with large amounts of rosin.

The analytical examination of shellac has been carried out more extensively in recent years, owing to the improved chemical methods which have been devised for the determination of adulteration, and because of a better understanding between buyers and sellers of the extent of this adulteration in the past.

The price of commercial shellac is dependent upon several conditions, chiefly its color, freedom from dirt, etc., as well as its content of added rosin, but the chemist is seldom called on to pass upon the purity of a given sample of shellac in other respects than the extent of its adulteration with rosin, and it is to the detection and determination of this substance in shellacs that improvements in methods have been mostly directed.

When the proportion of rosin present in admixture with shellac is large no difficulty is encountered, even by a person with small experience, in recognizing its presence through readily discernable physical properties, and its detection and determination in moderate amounts only, can be accomplished by chemical means with



reasonable accuracy and without any particular difficulty or uncertainty; but when the amount of rosin present is small, say in the neighborhood of one per cent or less it has not been possible hitherto to establish its presence in a complete and satisfactory manner by any of the tests that are generally well-known.

It is not my intention to review or even refer to all the various methods which have been proposed for the examination of shellac for commercial purposes, and after a few remarks on the so-called analytical constants of shellac and colophony, and some of the qualitative reactions by which the latter may be detected when in admixture, I shall confine my descriptions to those methods for its estimation in shellac which are at present most extensively in use in the United States, and which form naturally a prelude for the subject of the second part of the title of this paper.

“Analytical Constants” of:

|                                 | <i>Shellac</i> | <i>Rosin</i> |
|---------------------------------|----------------|--------------|
| Acid Number . . . . .           | 60–65          | 155–170      |
| Saponification Number . . . . . | 195–210        | 165–180      |
| Ester Number . . . . .          | aver. 150      | 0–12         |
| Iodine Number (Hübl) . . . . .  | 7–11           | aver. 125    |
| “      “      (Wijs) . . . . .  | 14–18          | “      228   |

As a means of estimating the extent of adulteration with rosin it will be readily observed that the determination of the iodine number has a decided advantage; the acid and ester values of a sample of shellac are useful as checks on the iodine absorption results, but owing to the limits of these values for shellac and rosin being nearer than in the case of their iodine numbers, they do not afford so useful a basis for calculation of the rosin present as the latter figure.

For the qualitative detection of rosin in admixture with other resins, the well known Liebermann-Storch reaction, which is the only one described in most books treating of the subject, has hitherto been almost exclusively relied upon for this purpose.

It is however, not very sensitive and besides has other disadvantages. Its limit of sensitiveness for rosin in shellac being about 2%, that is to say, shellacs yielding Wijs iodine values

below 22–24, may not give a positive reaction when this test is applied; so that until quite recently there has been no satisfactory way of confirming the presence of rosin in shellacs containing small amounts of it as indicated by the iodine figures obtained upon them.

There is, however, another qualitative test for rosin which is far more sensitive and reliable than that of Liebermann-Storch, viz:—Halphen's Color Test, which, as pointed out by Foerster<sup>1</sup> can be applied directly to shellac, best however, in the manner described by me in a former paper.<sup>2</sup> By this means using 2 grams of shellac and 15 c.c. of ether as little as 0.5% rosin can be detected without difficulty. Still smaller amounts may be detected by this reaction as I shall bring out later on in this paper.

Now we will turn to the methods of analysis which have found most favor in this country for the determination of the extent of adulteration of shellac with rosin, and first I shall refer to the Wijs-Langmuir Iodine method.

This process was originally suggested for use upon oils and fats by Wijs and later was adapted for use upon shellac by Langmuir<sup>3</sup> and more recently the method has been recommended, practically without change, by a committee of the American Chemical Society<sup>4</sup> as the most reliable of those in use up to the time of their report.

The process consists of the following procedure: 0–200 grm. of the finely ground sample is introduced into a dry 250 c.c. bottle with a ground stopper, 20 c.c. of glacial acetic acid of 99% strength is added, and the mixture may be warmed gently until solution is complete (except for the wax). A pure shellac is rather difficultly soluble. 10c.c. of chloroform is added and the solution cooled to 21–24°C. (72°F.); 20c.c. of Wijs solution is then added from a pipette with a narrow orifice. The bottle is closed and set aside for exactly one hour in a darkened place (Presence of considerable rosin will be revealed by solution having taken on a red-brown color). During the period the bottle should be

<sup>1</sup> Ann. Chim. Anal., 14, 14 (1909).

<sup>2</sup> Jour. Ind. & Eng. Chem., 3, 86 (1911).

<sup>3</sup> Langmuir, J-S-C-I, 24, 12 (1905).

<sup>4</sup> Jour. Amer. Chem. Soc. 29, 1221–27 (1907).

partially immersed in water, the temperature of which is carefully maintained at 72° F. At the end of the hour the bottle is removed from the basin and 10 cc. of a 10% potassium iodide solution added and the excess of iodine titrated immediately with N-10 thio-sulphate solution using starch solution as an indicator.

With a little practice the end-point is sharp, most of the coloring matter of the shellac being retained in the chloroform which has separated.

A blank determination should be made at the same time with 20 cc. of the acetic acid, 10 cc. of chloroform and 20 cc. of the Wijs solution. After obtaining the number, the percentage of rosin is calculated by means of the following formula:

$$X = \frac{100(M-S)}{R-S} = \frac{100(M-18)}{228-18}$$

"M" being the iodine number obtained on the sample examined.

When all the proper precautions are carefully observed, particularly as set forth in a recent paper by Langmuir and White (*J. S. C. I.*, 30, 786 (1911)), this method has given excellent results, and is of especial value, since in the hands of different analysts, after a little experience, closely agreeing results upon the same sample can be readily obtained.

The objections to the use of the process are, first, that it is likely to give results below the truth, and second, that the method of ascertaining the amount of rosin is an indirect one and any other substance having a high iodine figure will be counted as rosin; the rosin itself is not separated from the shellac and consequently cannot be separately examined for identification.

A process with this end in view has, however, been devised by McIlhiney.<sup>1</sup> It depends upon the fact that rosin is soluble in petroleum ether, while shellac is not. Although it is not practicable to extract the rosin from solid shellac with petroleum ether, the latter may be used to separate the two resins when they are dissolved in a suitable solvent. Such a solvent is absolute alcohol or glacial acetic acid, either of these solvents being miscible with

<sup>1</sup> *Jour. Amer. Chem. Soc.* 30, 867 (1908) and 7th Inter. Cong. App. Chem. Section 1-99 (1909).

petroleum ether. To the solution water is then added which causes a separation into two layers since the alcohol upon dilution is no longer miscible with the petroleum ether, and by further addition of water the shellac is gradually precipitated from its alcoholic solution. The petroleum ether carries with it the rosin, and the wax, which was contained in the shellac, provided sufficient petroleum ether was used to dissolve it, and also a small amount of some of the resinous constituents of the shellac itself. There are several methods which may be used to effect a separation of the shellac-wax from the rosin, but the most convenient is to treat the petroleum ether solution of the two with an alcoholic alkaline solution which removes the rosin and leaves the wax dissolved in the petroleum ether, from which it can be recovered and determined if desired. From the alkaline solution of the rosin the latter may be recovered, after the removal of the alcohol by evaporation, by acidifying and extracting the acidified solution containing the precipitated rosin acids with a solvent such as ether, separating the ethereal layer and evaporating off the solvent to obtain the rosin which may then be weighed.

The steps of the procedure may be briefly described as follows: 2 grams of the shellac is dissolved in 20 cc. of absolute alcohol or glacial acetic acid, with or without gentle heating. After cooling 100 to 300 cc. of petroleum ether, having a boiling point not higher than 80° C. are added in small portions at a time and with constant agitation. It is important that the addition of petroleum ether be made slowly and with stirring in order that the shellac which is partially precipitated after the first portions of the petroleum ether have been added may not carry out with it mechanically any of the rosin (or wax) contained in the solution. 100 cc. of water is then slowly run in, also with constant agitation. This causes the liquid to separate into two layers and ensures the complete precipitation of the shellac. The necessity for agitation during this stage is again to ensure the collection into the petroleum ether of all the rosin. The liquid is then poured off from the flask in which the previous operations have been conducted into a separatory funnel. The layers readily separate and the aqueous-alcohol layer is drawn off. The petroleum ether portion is washed with a little water, and may be filtered and



evaporated off for weighing the residue of wax and rosin. One procedure at this juncture is to titrate the rosin after solution of the residue in alcohol with N-5 or N-10 caustic alkali and phenolphthalein as an indicator. The average combining equivalent of rosin does not vary greatly from 346, the figure used for this titration in the Twitchell process for the estimation of rosin in admixture with fatty acids.

It is better, however, to proceed to an actual separation by treating the petroleum ether solution directly after transferring into a clean separator, filtering if necessary, with 25 cc. of N-5 caustic soda in 50% alcohol. By this means, after one or two treatments the rosin is completely extracted from the petroleum ether, together with traces of resinous matter from the shellac itself which were originally taken into solution in the petroleum ether. After drawing off the alkaline layer, and evaporating off the alcohol, the rosin is precipitated by acidifying the liquid with a mineral acid and extracting the precipitated rosin with either ether or petroleum ether, which after separation from the acid liquid in a tapped funnel is evaporated off and the residue weighed.

By this process it is practicable to actually separate, exhibit and examine by appropriate confirmative tests the rosin which has been added to the shellac as an adulterant.

As previously stated the petroleum ether dissolves traces of the resinous matter of pure shellac, and from my experience this always amounts to about 1%, and may amount to as much as 2%, consequently the mere obtaining of a weighable residue at this juncture is not absolute proof of the presence of adulteration; and in the case of the presence of only small amounts of rosin or certain other foreign resinous substances, it becomes necessary to apply some further reliable and characteristic test for its identification.

We now have such means at our disposal in the very sensitive Halphen color-test before referred to. By applying this reaction to the residue of the ethereal extract of the precipitated resin acids in the McIlhenny process in the manner described in my previous paper,<sup>1</sup> it is possible to detect without difficulty as little

<sup>1</sup> Jour. Ind. & Eng. Chem., 3, 86 (1911).



as 0.1% of rosin in a sample of shellac, when 2 grams has been used for the analysis, which is the usual amount taken in the McIlhiney method.

Although in the case of these extremely small amounts of rosin the processes involved for its positive recognition are somewhat tedious and require a considerable degree of careful manipulation, yet in certain cases it may be of importance to answer the question whether a particular sample of shellac does or does not contain rosin. In view of the sensitiveness of this test it would appear that there need no longer be any reasonable grounds for doubt or dispute as to whether a certain sample of shellac is or is not free from this foreign resin.



## BENZOL AND THE COAL TAR DISTILLATES AND THEIR APPLICATION IN THE PAINT TRADE

JOHN M. KLATZ

*Philadelphia, Pa.*

In a book written in 1867, by Charles F. Crockett, and recently published in conjunction with the English translation of Bottler's book on German Varnish Making by A. H. Sabin, there appears an N.B. following the formula for a furniture japan:

"However by using a portion of No. 1 Coal Tar Naphtha and less Benzine, this japan will mix with raw oil."<sup>1</sup>

Elsewhere in the little book he refers to No. 2 Coal Tar Naphtha, and in speaking about asphaltum paints, he very tersely remarks that No. 2 Coal Tar Naphtha may be used in place of Turpentine, in order to cheapen the mixture. No. 1 could be used to better advantage but is more costly. From this, when you consider that No. 1 Naphtha is a product similar to 90% water-white Benzol of this day, and No. 2 would correspond to the prevailing straw-colors, it will give some idea as to the relative costs of these two varnish and paint materials forty years ago as compared to now. It was necessary for Mr. Crockett to use a crude Benzol to have a price lower than Spirits of Turpentine, while for the past year, 90% water-white Benzol has been selling from one-fifth to one-half the price of Turpentine.

The strides that have been made by the producers of Coal Tar Naphthas are comparable with the demand from paint and varnish makers. This can be roughly figured when we consider that in Mr. Crockett's time two grades were known, No. 1 and No. 2; that is, refined and crude. To-day there are on the market ten refined Coal Tar Distillates ranging in boiling point from 82° to 200° C., and five crude fractions of approximately

<sup>1</sup> "German and American Varnish Making," Prof. Max Bottler of Wurzburg; Alvah Horton Sabin. John Wiley & Sons, New York.

the same range. The direct cause of this is the demand of the paint and varnish manufacturer on the tar distiller, and is definite proof that these solvents are much more in vogue than in the days when Turpentine was cheap and plentiful. For example, where Coal Tar Naphtha was used then in order to enable a japan to mix with an oil, no one would have ever employed a high boiling fraction to give a brushing quality or "length" to a varnish made with "short" thinners.

The era of the Benzols in the paint and varnish trade may truly be said to have begun with varnish removers. Of course, many manufacturers were well aware of the solvent power and the working qualities of Coal Tar Naphthas before that time, but there was a prejudice as to odor, and danger as to fire risk, so that the trade was loth to accept goods which smelled strongly of Benzol. But the introduction of the paint removers tended to familiarize people with the odors, and then, too, the use of crude gas drips and other very bad smelling hydrocarbons has made the refined goods smell quite pleasant by comparison. This has been a very good feature of this class of goods, which consume a very large percentage of the Benzol used by the paint trade; but there has been also another condition brought about by their vogue that is not so desirable. When the higher boiling Naphthas were first offered as paint materials, people were inclined to regard anything with Benzol in it as a paint remover. The reasoning is not sound, for the presence of oil or resin in Benzol inhibits its action on oxidized bodies, such as paint or varnish films.

The profitable handling of paint removers at a time when Linseed Oil, Turpentine, and most profitable paint and varnish materials were advancing, led to the seeking of other specialties, and a very large number of these newer materials are made with the use of some one of the Coal Tar Distillates. Probably one of the most generally known of these specialties is the penetrating stain. Benzol is employed as a solvent for oil soluble anilines in such instances.

This field, while dominated by three or four manufacturers, belongs essentially to the paint trade, and many painters make their own stains for each job; hence it is very hard to form an

estimate of the amount of Benzol consumed in these preparations, but from the consumption for 1909-10 & 11 of the principal manufacturers it has been possible to estimate an increase of 58% from 1909-1910, and from 1910-1911 65% represents the percentage increase. This increase is characteristic of the use of Benzols in the specialty lines, so that now the manufacturer of paints carries a much larger line, due largely to the versatility of Benzol. Where formerly the principal product was paint and varnish remover, we now find offered:

Oil Soluble Stains (Penetrating).

Enamels: Pigment in Damar Benzol Varnish and Asphaltum Benzol Varnish, as the stove pipe enamels.

Rubber Paints: Insulating proposition.

Spirit Varnish: Insulating & Shellac Substitute.

Flat Wall Coats: Wood Oil and Pigments.

Bronzing Liquids with varnish and cellulose bases.

Concrete Paints: Both the unsaponifiable gum and wood oil varieties.

N.B. "No attempt has been made to enumerate all the specialties in which Benzol is employed, as many are specialized products by certain manufacturers and while in many cases the suppliers are familiar with the uses, it was not considered fair to divulge them."

These few will serve as examples of the way that the manufacturers have made use of the various properties of the Coal Tar Naphthas. In each case selected it can be readily seen that the grade of Benzol is chosen for its particular properties. Strong solvent power, brushing quality, the slowness or quickness of evaporation, penetration or flash point have been considered in the choice.

This class of goods very likely consumes the bulk of Benzols in the paint trade, and next comes a line where some peculiar property is made use of to correct some defect in a material already in use. This for instance, is very strikingly seen in the use of turpentine substitutes of a petroleum origin. Here no Coal Tar Distillate can compete on price, yet many manufacturers who know their solvents well have been able to make use of the



solvent action and complete drying of Benzol by adding a small percentage, thus increasing the efficiency of their substitute, and not materially increasing the cost. This sort of thing is very often done in goods that tend to thicken or liver, and it can be considered very intelligent practice.

In almost this same class comes the only use of Benzol in a true paint that is a pigment ground in a suitable oil of a drying nature. Early in the use of the more modern woods in building it was advocated to let woods of a sappy and resinous nature such as cypress and yellow pine, go unpainted, but the use of panels unpainted on test fences soon changed this idea, and the problem was attacked from the painters' standpoint. It was found that if a suitable priming coat was applied little or no difficulty was experienced with the succeeding coat or coats. The addition of a small amount of Coal Tar Naphtha to the Linseed Oil of the priming coat was found to give the requisite penetration; but so far this has been rather the painters' specialty than the manufacturers', as the writer has never encountered but one prepared paint on the market intended for priming work of this sort.

It has also been suggested to use Benzol or higher boiling homologue in the priming coats of paints to be used on surfaces where mold and mildew are to be encountered, and thus employ the germicidal power of a Coal Tar Distillate, or use a Naphtha to convey a small percentage of phenol into the pores of the surface to be painted.

While as yet no data is available on this proposition, it is mentioned as one of the instances where the various Coal Tar Distillates are being applied to the paint problems of to-day.

## COBALT DRIERS

V. P. KRAUSS

*Long Island City, N. Y.*

The cobalt compounds which are generally offered on the market to-day, may be divided into two classes. In the first are cobaltous Oxide, Acetate, Sulphate, Chloride, Nitrate, Hydroxide, and Basic Carbonate. In the second class, are various grades and qualities of resinates (sometimes called sylvinates), both fused and precipitated, oleates or linoleates, oleo-resinates, tungates and resino-tungates, besides some other liquid preparations composed in whole or part of the foregoing.

From the varnish manufacturer's standpoint the substances in the first division are crude materials which are utilized in the production of the compounds in the second class, and also in the preparation of some varnishes, liquid driers, drying oils, and the so-called paint oils. The materials enumerated under the second class, are the result of a varnish maker's labor, and when properly made and used in mixtures to which they are adapted, give very good results.

The inorganic salts of cobalt do not directly come under the scope of this paper, and thus will not be directly considered except inasmuch as their use as crude material affects the driers into whose composition they enter.

It is only within the past year that the cobalt driers have been offered to the American paint and varnish manufacturers. Up to the present time, their use is not general, first, because of the very high price, and second because their use is not thoroughly understood and many experimenters have had unsatisfactory results and therefore refused to further consider the introduction of the new material. Furthermore, not all of the cobalt driers, whether liquid, paste, or solid, now offered for sale are properly made and truly adapted to the purposes for which they are recommended. This situation in addition to unsatisfactory results

obtained by some of those experimenting, would naturally have a retarding effect on the introduction of a new type of material.

The salts of cobalt which are at our disposal in commercial quantities, are all of the cobaltous or divalent type. It has been found that although they can be readily used in the manufacture of driers and worked like the various compounds of manganese, lead, zinc, calcium, aluminum, etc., the organic compounds formed, which are the basis and active principles of the so-called driers, are not efficient while in the cobaltous state. The cobaltic combinations however, are very active driers, and it is for the formation of trivalent cobalt compounds that we strive in the making of driers. This transformation can be effected in several ways. By blowing cold, heated, or ozonized air through the hot cobaltous drier stock, or by the introduction of liquid or solid oxidizing agents. The use of cold or even heated air is a very long and tedious operation if carried out to the extent to which it is necessary in order to get the maximum strength in the drier, and greatly adds to the cost of an already expensive material. The use of the liquid or solid oxidizers can be carried out successfully and in a comparatively short time, although even when great care is exercised the batch of material is in danger of catching fire.

Since driers are used in a number of industries in which drying oils form part of the material produced, and since the operating methods of the various manufacturers are widely divergent, the siccatives or driers adapted to each will in many instances show widely different characteristics, not merely in form but also in composition.

Since the paint manufacturer and also the practical painter who mixes his own paints from paste colors and raw or treated oil, are the principal consumers of what are generally known as driers, the materials adapted for their use may be first considered. The driers will in practically all instances, be in the liquid state either very fluid, of heavy consistency or of a semi-paste nature. In composition, they will mostly consist of resinates, tungates, oleates, or linoleates, or combinations of the three. For the drying of linseed oil, when the proper driers are selected, little or nothing can be asked in addition to those known at present.

When the general lead, manganese and other prevalent metallic driers are well chosen raw linseed oil can without any difficulty be made to dry by the addition of from 5 to 10% or even less, the time of drying under average weather conditions being from 10 to 24 hours. By the use of cobalt driers, the same drying effect can be obtained when only from 1 to 3% of a liquid drier is used. I am not yet prepared to say positively what the ultimate effect of cobalt driers is upon paint films, but from my experiments, I am led to believe that cobalt has not the harmful progressive oxidizing action that some of the usual manganese lead compounds have. It has also been noticed that although a cobalt drier may be fairly dark in color, it will not have as darkening effect as one of the usual driers of like color would have upon a white paint. The cobalt driers likewise, show the same phenomena as some of the others when used in excessive amount; that is that although the paint film will set up well in the usual time, the drying action apparently reverses and the film remains tacky.

The terms applied to liquid driers are often uncertain and apt to be misleading. There are no general standards for strength or consistency, and, it must be admitted, many of the materials found on the market contain more volatile thinners than is conducive to obtaining a maximum drying effect with a minimum quantity of drier.

The value of the Cobalt specialties depends not on their power to dry Linseed Oil, but on their ability to make the lower priced semidrying oils act like it.

Soya, Fish, and even Corn and Cottonseed oil are adaptable for use in paint, and when correctly treated increase its durability. Dr. Maximilian Toch has published the results of his extensive research and experimental work with both Fish and Soya Oils, and there describes the types of driers suitable for them.

In the making of waterproof fabrics, insulating coatings, etc., both liquid and solid driers are used. In the linoleum, oilcloth, patent leather, artificial leather and similar industries, the semi-liquid, paste, and solid driers are in demand since for these products the manufacturers cook the oils and varnishes in their own factories.

The paste and solid driers must essentially be considered under



the caption of crude materials because they must be churned or cooked in the oils or varnishes in which they are used.

The methods of making both the solid and liquid driers are in general similar in the first stage of the process, and thus may be described under the same headings.

#### *Resinate of Cobalt; Precipitated and Fused.*

This is correctly made by saponifying rosin or colophony with caustic soda or sodium carbonate, care being taken to avoid an excess of the reagent, and then precipitating with a solution of some salt of cobalt. The chloride or sulphate serve best for this purpose. The precipitated resinate, or as it is sometimes called, rosinate or sylvinate, must then be thoroughly washed, and then pressed and dried. This will yield a pinkish fairly fluffy powder when ground, which will readily dissolve in oil at a low temperature. The fused variety is made by melting the dried resinate in a kettle and then pouring into cooling pans. The operation is performed more rapidly by taking the cakes from the presses and driving off the water and fusing in one operation.

#### *Cobalt Oleates or Linoleates.*

The basis of this class is generally linseed oil, although Walnut, Perilla, Soya, and some other oils may be used. The oil is thoroughly saponified with caustic soda and like the resinate, precipitated with a salt of Cobalt. The material is then carefully washed and pressed. It may be melted to form a dark viscous heavy fluid.

Several samples of cobalt linoleate which I examined consisted of bodied linseed in which small amounts of inorganic cobalt salts had been dissolved. Another was of the same order with the addition of volatile solvents.

True linoleate of cobalt, when fused with varnish gums and dissolved in volatile oils, yields an excellent drier.

#### *Oleo-resinates.*

This type of drier is made by melting together the precipitated resinate and linoleate, sometimes with the further addition of fused fossil gum-resins.



### *Tungate of Cobalt.*

Like the linoleates, the tungate of cobalt is made by saponifying pure China Wood Oil (Tung Oil) with caustic soda, care being taken to avoid excess of caustic, and then precipitating with a salt of cobalt. The tungate is then washed thoroughly, pressed and generally dried and fused. Great care is necessary in the preparation of a tungate since it oxidizes very rapidly, and the oxidized material is useless.

Like the linoleate of cobalt, the tungate may be fused with the resinate to form what may be called a resino-tungate.

In general the foregoing substances are incorporated in oils by means of heat, the combining temperature being between 300° and 500°F. The amount necessary will vary from about 1-2% to 5 %. In order to make *liquid driers*, the paste or solid driers can be melted alone or in combination with gum-resins, bodied linseed oil, or both, and then thinned to liquid consistency with volatile oils.

Among other cobalt salts, some of the chemical manufacturers offer the acetate, with directions for its use as a drier. All agree that between two and four tenths of one percent are necessary to dry linseed oil. The oil should be at a temperature between 300° and 400°F., and be carefully stirred until all the salt is dissolved. Soya and China Wood Oil may be similarly manipulated.

It is still a little too soon to make a positive statement as to how oils thus treated with the acetate withstand wear and exposure.

Cobalt Oxide, like the Acetate, can be directly added to oil during boiling. It however dissolves slowly and necessitates heating to high temperature; the resulting product is also very dark, and mostly consists only of bodied oil. Rosin also will directly combine with cobalt compounds on heating together in a suitable kettle or container. The product possesses a number of objectionable features. It still is mostly unchanged rosin, has become much darker and lost considerably in weight due to volatilization. I have tried the effect on oils of quite a number of Cobalt compounds, but found none equal in efficiency to those described in the foregoing.



# THEORY AND PRACTICE OF THE PAINTING OF THE MODERN STEEL PASSENGER CAR

BY J. W. LAWRIE  
*Pullman, Illinois*

Since the very general introduction of the steel passenger car into our railway service, new problems in painting and preservation of the steel have been brought to our attention. It is true that the problem of the preservation of steel is not in itself new to us, but the artistic preservation and protection of steel from corrosion, etc., is a new problem. A railway passenger coach must not only be painted carefully, but it must be painted so as to present a pleasing appearance to the eyes of the traveling public. This effect is arrived at by the color, lustre, harmony of color, etc., and thus some of the pigments which have great value for steel protection cannot be used, and others that do not have merit for steel protection must be used merely on account of the color they possess. The railways in general have retained the same standard colors for steel cars that they had for wood cars. The consideration of the protection of steel has been secondary to the color of the finished coach. Fortunately, this consideration has not been felt for certain colors, because we have found good inhibiting pigments which harmonize with the color desired and afford good protection to the steel.

Paints for steel have different functions, in many respects, than those for wood. In painting steel we do not have the absorption into the pores, but to only an extremely limited extent, compared to that which we have in painting wood. For this reason there must be some other way adopted for getting the strong clinging effect that the pores of wood afford as an anchorage for the paint coats. Once we have the priming coat well anchored, the subsequent coats, if properly made and well applied, anchor themselves one on the other, all finally depending for their adherence on the fastness of the priming

coat and the strength and elasticity of the paint film. With steel we have only to a very limited extent inter-crystalular crevices, most minute in size and depth. These do not afford a firm anchorage, nor is the penetration of the paint into these crevices of much value for anchorage. Sandblasting steel gives a slightly roughened surface, which aids materially in holding the paint to the steel. It is almost necessary to assist an oil paint with something which is a better adherer to steel than linseed oil. This we find in varnishes. For this reason we find in all steel primers a certain amount of varnish. At the same time the pigments which have answered for wood may or may not do for steel. Depending on the color, we may have more or less pigment to get proper opacity, for dark colors less, for light colors usually more pigment is necessary than in the paints used for wood. It has been established in a practical way, as well as experimentally, that the fewer the number of paint coats on steel which will give the maximum protection the longer wearing and better service will the paint coating give.

In general, we can functionate the properties of both the pigment and the vehicle for painting steel.

The pigment must give us the color and shade desired, opacity, thickness of film; it affects the life of the paint, both by its actinic action due to its color absorption, etc., and its chemical effect on the oils or vehicle. It should be such as to give the maximum inhibition of corrosion on the steel.

Corrosion itself may be due to several factors. Moisture must be present for continuous corrosion, acid gases and oxygen assist, and any free acid, such as is used in pickling steel is a strong inducer of corrosion. When we consider these causes, then we can attempt to get ways of overcoming the effects of these causes and so approach perfect inhibition of corrosion. It must be borne in mind, however, that inhibition of corrosion is only one of the desirable qualities of a paint for steel.

The vehicle has for its fundamental functions, the binding of the particles of pigment together, and the cementing of this bonded material onto the steel surface. It gives life to the paint and gives the finish effect desired as to lustre, etc. It must also

be such as to exclude from the steel surface all moisture and gases.

Both pigment and vehicle have additional functions other than those given. These mentioned are the ones of greatest consideration in the study of proper paints for steel protection.

There are essentially two or perhaps three great classes of pigments as regards their effect on steel. These classes can be called the Electrical, the Chemical and the Passifiers. Examples of the passifiers are the Chromates, which seem to render the steel immune to oxidations.

In line with the electrolytic theory of the corrosion of steel, the differences in electrical potential produce a current of electricity in the direction of the high to low, or also positive to negative. The different pigments show such differences in their relation to steel, and for this reason if we use pigments which are positive to steel, then in any flow of current we would have the positive material going into solution and the negative material, or, in this instance, the steel, protected. Such pigments would therefore be inhibitors of corrosion of steel. Those of the same potential, or neither positive or negative to steel, would be neutrals and those negative would be accelerators.

The chemical pigments are those which through their particular chemical properties, such as acidity, either direct or through hydrolysis, neutrality, or alkalinity, affect the steel so as to inhibit or accelerate corrosion. It is practically established that there is a minimum alkalinity below which there is no inhibition, and also with too strong alkalinity the action of the pigment on the vehicle oils is so pronounced that such pigments are detrimental to the life of the paint. Practically all pigments belong to both the electrical and chemical classes. A pigment may be positive to steel, and yet in itself or by hydrolysis be so acid in action that instead of being, as we would expect, an inhibitor, it is instead, a strong accelerator of corrosion. In the same manner, a negative pigment may be sufficiently alkaline as to become an inhibitor. Many pigments are both positive and alkaline, and therefore extremely good inhibitors. Others are neutral, either through opposing electrical and chemical properties (as applied to inhibition, etc.), or are neutral of them-



selves in all respects. Again, other pigments are negative and acid, and so strong accelerators. There are, of course, all grades and stages in these valuations. It is, however, possible by test to identify the different properties of the different pigments and combinations of pigments, and so classify them as to their actual value for inhibiting corrosion.

The knowledge of these classes is worth having, but not of great importance, unless we have satisfactory methods of determining to which class each and every kind of pigment or mixture of pigment belongs. It is possible to measure directly differences in potential between pigments and steel, and also the relative acidity or alkalinity, either as a direct property or as one produced by hydrolysis. These tests can be applied directly to most pigments, but not to all. There is one test which can be considered final and fair. That is, an actual exposure test of the pigments combined into paints and applied to steel panels under differing exposure and weather conditions. It must be admitted at once that such tests are not absolute, but their relative value cannot be disputed. It is impossible from the results of such tests as those at Atlantic City to say that the American Vermilion is 10 times as good a pigment as some other pigment which would be rated at 1. The relative fact is that American vermilion is a first-class inhibitor of corrosion, whereas the paint rated at 1 is not an inhibitor and is probably one of the negative pigment paints, and therefore an accelerator. It is extremely tedious, however, to wait four or five years for such an exposure test to give reliable results. Events and truths in paint grinding history are moving much too fast and some other means must be had for testing out these pigments and vehicles in a shorter time and yet with a reasonable amount of assurance that the results so obtained check up the actual exposure or railway service wear.

I have been experimenting for a long time with the so-called razor blade test for both pigment and vehicle. The test is made by completely separating the pigment from the vehicle by solvents and the centerfuge, so that there is no trace of the vehicle left with the pigment. The pigment is then re-ground until all of it passes through a 100-mesh sieve. It is then made

into a stiff paste, with water, spread out on a square of filter paper and the emiered razor blade is wrapped up in the pigment in such a manner that the pigment is in intimate contact with the surface of the blade all over. Here is where many fall down on the test. The wrapping up of the blade properly has much to do with the success of the experiment. The blades are now left for about 21 days, being kept moist all the time. They are then cleaned, re-weighed, and the loss in weight, together with the appearance of the blade, give the value of the pigment for steel protection. I have followed the results so obtained with outdoor exposure panels, and have seen the conclusions arrived at from the razor blade test check with wonderful accuracy the results obtained on exposure. As examples of these checks I give the relative values placed on some of the Atlantic City steel panels and the losses on the razor blades:

|                          | Loss Razor Blade | Atlantic City<br>rating |
|--------------------------|------------------|-------------------------|
| American Vermilion.....  | .0005            | 10                      |
| Sublimed White Lead..... | .0015            | 9                       |
| Corroded White Lead..... | .0247            | 2½                      |
| Red Lead.....            | .0003            | 9                       |
| Zinc Chromate.....       | .0004            | 9                       |

I have made these tests on over 200 different pigments and mixtures of pigments, with the exposure test for a check. The results indicate that when properly carried out the blade test is reliable and of great value where time is such an important factor as in large testing laboratories.

In like manner the vehicle can be tested for its value as a resister of moisture and gases. The emiered and weighed razor blade is dipped into the separated vehicle and given two coats, with proper drying intervals. The blade is now subjected to alternating treatments with water and moist sulphur-di-oxide, and carbon-di-oxide gases. This treatment is continued for a period of eleven days. The blades are then cleaned and re-

weighed. The appearance and loss in weight give the relative value of the vehicle as a resister of moisture and gases. Here we also use the filmometer with great success. This particularly where we are called upon to test paints from competing companies, and designed for the same purpose. The test of the resistance of the film to acid and gas penetration is of extreme importance. We have in railway service to contend with sulphur-di-oxide and carbon-di-oxide gases, as well as an almost continuous presence of moisture. For this reason the paint must be able to exclude these gases and moisture. This exclusion depends largely on the nature of the vehicle. Straight linseed oil or soya bean or other like oils will not exclude completely. If, however, we add a gum varnish to the oil the porosity is largely stopped. This, of course, is more or less perfect, according to the amount of varnish used, its kind, etc. At the same time the physical condition of the pigment must be considered, as too coarse a pigment will practically always leave a porous film. Too much varnish on the other hand, especially in a priming coat, will leave a glossy surface, to which the second coat will not adhere well. At the same time it is well established that varnish will not carry a large amount of pigment and give successful outdoor surface. It is for this reason that there have been so many failures with the so-called "quick process methods" of finishing steel cars.

We have made many tests to establish the value of baking the paints on steel cars. Our results, and practical experience, based on these tests, has shown that the life of the baked paint on steel is prolonged wonderfully and also the adherence to the steel itself is very much better. At the same time the baking has the additional value of making the vehicle much more impervious to moisture and gases than the same vehicle unbaked. Numerous experiments with certain kinds of vehicles baked gave a resistance in this way of almost three times that of the same vehicle unbaked. The mechanical difficulties of baking an entire car are large. We are at the present time experimenting in this direction. In this respect, the removable sheathing of the modern Pullman is of a decided advantage, as it can be readily taken off, the paint removed, the sheathing re-painted, baked

and placed back again on the car as before. There are some other difficult problems involved in the baking of the paint. It is the best practice at the present time to bake the surfacer. This baking produces an extremely hard and brittle coat. Up to the present, when it is necessary to refinish such a car, we have not found any chemicals which will successfully remove this baked surfacer. It is, however, possible to remove all coating over the surfacer and then rebuild up again in the regular manner. Here again the problem of baking the entire car is paramount and so far we have not solved the problem with entire success.

The baking temperature and length of time baked have a great deal to do with the life service of the paint. There is, for most vehicles, a minimum heat necessary to produce the internal changes in the vehicle, which give it the valuable properties so desired. This change has also a time factor. In general, the lower the temperature and the longer the time the paint is baked, the better the wear, service and resistance to moisture, and the more elastic the film. Twelve hours at 180 deg. Fah. are better than five hours at 280 deg. Fah.

There is no longer any argument with regard to the preparation of the steel for painting. Wherever possible sandblast. Pickle only when no other means affords itself to remove scale and rust. Pickling with sulphuric acid gives under our usual factory methods the best accelerator of corrosion of any agent met with in regular railway service. Capillary attraction is an extremely powerful force. The sulphuric acid by this force enters the spaces between the crystals of the steel and is held very tenaciously. A mere dipping in a bath of water or several baths of water fails to remove all the acid and with the hygroscopic nature of sulphuric acid an ever increasing area of steel is subjected to acid action. The whole sheet begins to corrode under the paint coat. Even with a paint which is inhibitive and moisture-proof such action will soon destroy these valuable properties. The action of the acid is cyclic and almost unending. Ferrous sulphate is readily converted to ferric sulphate and with moisture to ferric hydrate. Under these conditions the ferric hydrate is precipitated out of solution and does not re-act further with the acid. The acid is re-generated and again re-acts with



the steel, etc. The ferric oxide formed is electro negative to steel and with moisture and acid a current is established, carrying iron ions from the steel into solution. These are precipitated out as more ferric hydrate or oxide and so again the action proceeds ad infinitum. I would rather pickle with hydrochloric acid than with sulphuric acid even at a higher cost, because this acid is not hygroscopic; it is volatile at a low temperature and its capillary force is small compared to that of sulphuric acid. It can therefore be washed out with greater ease and sureness and can ultimately do less harm if not entirely obliterated. If you have to pickle with sulphuric acid, then wash with a stream of hot running water, so as to overcome by heat, force and dilution the capillary strength of the acid. Treat with lime water and wash again, dry and oil.

There is one feature of steel car building that is generally neglected. The outside surface of the steel is taken care of in a more or less respectful manner, but the inside of the sheet is usually given a coat of slush paint and the scale is seldom removed. Oil may be on the surface, or rust already formed. This treatment is certainly to be condemned. The inside of the outside and the outside of the inside sheets form a box with little ventilation, but usually holding a great deal of moisture. The paints used are seldom good resisters of moisture, and as a result corrosion starts and is aided by the conditions until there is often danger that the inside of the sheet will corrode through before the paint on the outside has seen decent service. As color is of no interest in this case it is easily possible to apply a good inhibiting and moisture resisting paint on these unseen sides of the sheets of steel and so prolong the life of the car very much. It is also a matter of general safety to properly paint this material, as it is impossible to get at the surface for repainting after the car is in service.

Where moulding abuts on steel sheets it is usual to interpose sheet copper between the two pieces of steel. This is to produce as near a water tight joint as possible. The fact remains that the joint is never entirely water tight. Copper is electronegative to steel and the steel therefore goes into solution and rapid destruction takes place. I have seen siding renewed on many



cars in less than 9 months, and the destruction could be traced directly to this electrolytic effect. Aluminum on the other hand is electro-positive to the steel and so it goes into solution and saves the steel. It soon coats over with oxide and thus the reaction is largely diminished. The steel itself is entirely protected. This substitution of Aluminum for copper was made entirely as a result of the electrolytic theory and the test of its worth by means of the well-known ferroxyl agaragar test of Cushman, Gardner and Walker. The copper in contact with the steel in the agar jelly caused the flow of current and the liberation of iron ions, which with the ferri-cyanide gave the characteristic blue-green color. With the aluminum under the same conditions there was formed the pink, due to hydroxyl ions and the white aluminum ferricyanide.

There are several essential properties which should be possessed by the different kinds of paint used on steel. The usual procedure is first, sandblast, next prime, and following usually a second but different primer; then filler and surfacer, color and varnishes. The essentials of a good first primer or first coat of paint on steel are that it adhere well to the steel, present a good surface for the second coat, and that it have a pigment that is a good inhibitor of corrosion. It is not essential that the vehicle be altogether gas and moisture proof, although it is better so. The second coat should adhere well to the first one. It should be primarily a paint that is a good excluder of gases and moisture. It does not have to have a strongly inhibiting pigment, but it is better with such a pigment. It is usual after the application of the fillers and surfacers to rub down to a smooth finish with water and pumice. This treatment requires undercoats, which will resist the water and next to the steel a pigment that will prevent corrosion, even if some moisture gets through the outer coats. It has been possible to get better results from two coats instead of a single primer combining all qualifications. It is more practical also to get the resistance to moisture by making both coats moisture proof than by depending on the second coat alone.

The fillers or surfacers are designed to give a film such that it can be rubbed down to a smooth surface without tare and

still be flexible. Most of them are fairly brittle and all of them are hard. The brittleness is increased with the baking. It is, however, possible to make a surfacer which will be hard enough to rub well and still be very elastic. Such an elastic surfacer will give to the paint coats as a whole, much better wear and freedom from checking than a more brittle and non-elastic surfacer. The coats of color, etc., following the fillers are never or seldom baked. It is very difficult to hold the shades and finish constant when we bake the finishing color coats and varnishes.

I have tried to show the theory of steel car painting as it has been applied with some success in a practical manner on a large scale. We are using the tests and theories described every day and with increasing confidence in their practical value. There are still many new phases of the work to be thought out and problems to be solved. We need more men with a little time for the practical theoretical work of the proper protection of the steel passenger car.

## KÖNNEN ANSTRICHE ROSTFÖRDERND WIRKEN?

VON ERIK LIEBREICH

*Berlin, Germany*

Die Ansichten über die Entstehung des Rostes auf Eisen haben in den letzten Jahren eine grosse Umwandlung erfahren. Früher führte man die Entstehung dieses für die Eisentechnik so gefährlichen Feindes einzig und allein auf chemische Angriffe zurück: man nahm an, dass der Sauerstoff der Luft das Eisen zuerst oxydierte und alsdann hinzutretende Feuchtigkeit zur endgültigen Bildung von  $\text{Fe}(\text{OH})_3$  führte. Auch wurde—wie sich später zeigte—irrtümlich angenommen, dass die Anwesenheit von Kohlensäure zur Bildung von Rost notwendig sei. Heute, wo die Chemie physikalischer, wenn ich so sagen darf, geworden ist, oder wo Chemie und Physik Hand in Hand Probleme in Angriff zu nehmen anfangen, haben die Anschauungen über die Ursachen des Rostens eine völlige Neugestaltung gefunden.

Vorbereitend für diese Umwandlung war die von Arrhenius aufgestellte Lehre der Jonenspaltung von Electrolyten und die von Nernst gegebene Theorie des Lösungsdruckes. Die Früchte, die die Electrochemie seitdem pflücken konnte, gehören zu den schönsten Errungenschaften der physikalischen Chemie. Eine Anwendung dieser neuen Anschauungen auf das Problem des Rostens speciell fand erst verhältnissmässig spät statt. Die wohl von Fechner zuerst aufgestellte Theorie der Lokalströme, welche die schnellere Auflösung von Metallen, wenn diese edlere Verunreinigungen enthalten, dadurch erklärte, dass sich zwischen dem eigentlichen Metall und der verunreinigten Substanz electrolytische Prozesse ausbilden, welche die dabei anodische Grundsubstanz in Lösung gehen lassen,—diese schon in Vergessenheit geratene Theorie wurde wieder aufgenommen, und, weiter geklärt durch die modernen Anschauungen des Lösungsdruckes, auf das Rosten des Eisens angewandt. Hier gebührt vor allen den amerikanischen Forschern Cushman und Gardner das Ver-

dienst durch ihren Ferroxyl-Indicator und die damit angestellten Untersuchungen einen strikten augenfälligen Nachweis der electrolytischen Lokalstrom-Theorie erbracht zu haben. Man darf wohl sagen, dass die Zahl der Gegner dieser Theorie von Tag zu Tag abnimmt, obgleich man sich darüber klar sein muss, dass es besonders in der Industrie deren noch eine ganze Anzahl giebt; die Ursache hierfür mag wohl vor allem darin zu suchen sein, dass Verständniss und Interesse für die physikalische Chemie hier oft genug fehlen und dass die schon oft als falsch bewiesene und doch immer wieder auftauchende Ansicht, dass die Farbe nur zu decken braucht, um vor Rost zu schützen, der grösste Feind jedes Fortschrittes auf diesem Gebiete ist. Man muss mit Bedauern konstatieren, dass die Industrie der Rostschutzfarben, von einzelnen Ausnahmen abgesehen, hinter der wissenschaftlichen Forschung weit zurückgeblieben ist; sie befindet sich hierin im scharfen Gegensatz zu der organischen Farbenindustrie.

Mit der bisherigen Formulierung der electrolytischen Theorie haben die Rostvorgänge von Eisen, welches sich in feuchter Luft oder in einem Electrolyten befindet, eine völlig erschöpfende Erklärung gefunden. Anders scheint es mir jedoch zu sein, wenn man den Ursachen der Rostentstehung unter Anstrichen nachgehen will. Es scheint mir, dass hier eine Erweiterung der bisherigen Theorie notwendig ist, welche sich wohl am einfachsten in der Frage zusammenfassen lässt: Kann man die electrolytische Theorie auf das System Farbe Feuchtigkeit Eisen ausdehnen? Es ist über diese Frage schon Manches geschrieben worden, doch ist es zu einer Klärung vorderhand noch nicht gekommen, zumal die bisher für diese Frage angestellten Versuche physikalisch nicht immer einwandfrei sind.

Wenn man ein Stück Eisen mit einer Farbe bedeckt, so haftet die Farbe nicht an allen Stellen des Eisens. Es lässt vielmehr die dem Eisen zugewandte Seite der Farbschicht kleine Vertiefungen oder Höhlen frei. Hiervon kann man sich am besten überzeugen, wenn man z. B. eine Farbe auf Glas streicht, und dann mit der Luge bei günstiger Beleuchtung betrachtet, oder wenn man ein Zinkblech streicht, welches man nachher in starker Salpetersäure auflöst, so dass man die Farbhaut frei erhält. Diese kleinen Höhlen werden sich wohl zweifelsohne in einer



zum Teil von den äusseren Umständen abhängenden Zeit mit Feuchtigkeit anfüllen, da bekanntlich Feuchtigkeit und Wasser von der Farbhaut aufgesaugt werden; man hat wegen dieser Eigenschaft auch die gestrichene Farbe schon mit einem Schwamm verglichen. Aber selbst, wenn im wesentlichen eine Zufuhr von Feuchtigkeit von aussen nicht stattfindet, so kann solche in diese Hohlräume bei dem Trockenprozess des Leinöls gelangen, worauf ich kürzlich hingewiesen habe,<sup>1</sup> da ja das Leinöl während seines Trockenprozesses fortdauernd Wasser abspaltet.

Eine ähnliche Annahme, wie die des Bestehens kleiner Hohlräume, werden wohl diejenigen Autoren, welche sich mit der Frage eines electrischen Stromflusses zwischen Eisen und Farbe befasst haben, stillschweigend auch gemacht haben, wofern nicht in besonderen Fällen anzunehmen ist, dass sich die ganze Farbhaut vom Eisen teilweise durch dazwischendringende Feuchtigkeit abhebt.

Die Möglichkeit des Vorhandenseins eines Electrolyten ist also gegeben. Die weiteren Fragen wären, ob Potentialdifferenzen bestehen, wo dieselben liegen, welches ihr Vorzeichen ist und endlich, ob die Widerstände, die in Betracht kommen, so gross sind, dass sie einen Stromfluss verhindern.

Was die Potentialdifferenzen anbelangt, so können dieselben möglicherweise, wie beim ungestrichenen Eisen, innerhalb des Hohlraumes zwischen zwei verschiedenen Stellen des Eisens selbst bestehen.

Für diesen Fall, der wegen der Kleinheit der Hohlräume unwahrscheinlich ist, wäre die ganze Frage auf die ursprüngliche Theorie zurückgeführt.

Anders jedoch, wenn Potentialdifferenzen zwischen dem *Eisen* und der *angrenzenden Farbe* bestehen!

Man unterscheidet hier am besten wohl folgende Möglichkeiten: Erstens die Potentialdifferenz entsteht durch Polarisierung; zweitens zwischen Leinöl und Eisen bestehen aus irgend welchen Ursachen schon an sich Potentialdifferenzen; drittens zwischen Eisen und dem in das Leinöl eingebetteten Farbkörper bestehen Potentialdifferenzen und haben die Möglichkeit sich geltend zu machen.

<sup>1</sup> E. Liebreich u. F. Spitzer Zeitsch. f. Electrochemie 1912, p. 24.



Der erste Fall wurde von den Herrn Walker und Lewis<sup>1</sup> an Conservenbüchsen beobachtet und die Ströme coulometrisch gemessen, die zwischen mit Leinöl, Lacken, Farben etc. bestrich-  
enem Eisen und reinem Eisen fliessen. Die genannten Forscher nehmen an, dass die meist porösen Lacküberzüge, die ungesättigte Verbindungen enthalten, auf den naszierenden Wasserstoff durch Absorption depolarisierend wirken und so Spannungsdifferenzen zwischen lackfreiem und lackiertem Eisen herbeiführen. Ob diese Erklärung ausreichend ist, mag zweifelhaft erscheinen, da die einzelnen Farben, welche doch sämtlich Leinöl enthalten, in diesem Falle gleiche Strommengen hätten liefern sollen. Jedenfalls bleibt aber die interessante Tatsache bestehen, dass messbare Ströme zwischen dem lackierten und unlackierten Eisen flossen.

Hieran schliesst sich zugleich die zweite Frage an, nämlich die, ob etwa zwischen Leinöl an sich und Eisen Potentialdifferenzen bestehen. Zu diesem Zwecke habe ich versucht die Potentialdifferenzen einer mit Leinölfirnis überzogenen Glasplatte gegen Eisen zu messen. Die Versuchsanordnung war dabei folgende: Die Firnisplatte tauchte in ein Bassin ein, welches mit dem Electrolyten gefüllt war, sie wurde an einer Klemmschraube aus Messing so befestigt, dass einige Centimeter der Platte bis zur Klemmschraube frei über der Flüssigkeit herausragten; zwischen Messing und Platte wurden kleine Eisenplättchen zwischengelegt, um bei etwaigem kapillarem Aufstieg des Electrolyten bis zur Klemmschraube keine falschen Potentialwerte zu erhalten. Eine Eisen-Electrode befand sich in demselben Bassin der Firnisplatte gegenüber. Die Messungen wurden mit einem Quadrantelectrometer (1 Volt = 17,4 cm) ausgeführt. Als Electrolyt im Bassin wurde eine schwach mit  $\text{H}_2\text{SO}_4$  angesäuerte 1-10 n-KCl Lösung genommen. Die Messung gegen eine Eisenelectrode aus gewalztem Blech, das noch teilweise Hammerschlag hatte, ergab folgendes Bild: Im ersten Moment trat ein Ausschlag von ca. -17,5 cm = ungefährt -1,0 Volt, ein (das Vorzeichen bezogen auf die Leinöl-Electrode), und zwar so, dass das Eisen positiv, d.h. edel im Vergleich zu der Leinöl-Electrode war. Dieser Ausschlag ging alsdann unter starkem Schwanken bis auf

<sup>1</sup>W. H. Walker u. W. K. Lewis Journ. of Ind. and Engn. Chem. 1. 754. 1909.

im Mittel  $-\frac{1}{2}\text{cm} = -0,03$  Volt zurück und stellte sich dort eine Zeit lang ziemlich constant ein, um dann gegen O zu tangieren. Ähnlich war das Bild mit einem frisch geschmirligten dünnen Eisendraht. Der erste Ausschlag betrug ca  $-22\text{cm} =$  ungef.  $-0,125$  V, und tangierte dann, nach einem Aufenthalt bei  $-2\text{cm} = -0,11$  Volt, wieder gegen O. Man kann wohl in Anbetracht dieser Resultate vielleicht sagen, dass das Leinöl sich als schwach rostschtützend erweisen kann, wenn auch die zu gunsten des Eisens auffallenden Potentialdifferenzen in ihren endgültigen Werten äusserst gering sind und praktisch nicht in Frage kommen dürften. Welches der Vorgang an dem Leinölfirnis ist, ob ein chemischer oder physikalischer, darüber kann man sich ohne Weiteres kein Bild machen.

Die ersten hohen Potentialdifferenzen, die man nach dem Eintauchen der Platte beobachtet, deuten darauf hin, dass sich die Leinöl-Electrode im ersten Augenblick wie eine Gas-Electrode verhält. Es scheint demnach, dass wenn Ströme zwischen einer mit Leinöl bestrichenen und einer unbestrichenen Eisenplatte beobachtet werden können, die Ursache hierfür, wie die Herren Walker und Lewis annahmen, tatsächlich in irgend einer Polarsiationserscheinung zu suchen ist. Zwischen dem Leinöl an sich und dem Eisen bestehen, wie ja auch von vorneherein anzunehmen ist, keine Potentialdifferenzen; das Leinöl ist eben indifferent.

Verschiedentlich wurde—um auf die dritte Frage zu kommen—in der Praxis und in der Litteratur die Vermutung ausgesprochen, dass zwischen Farben und Eisen Potentialdifferenzen bestehen; besonders wurde dies von der Bleimennige behauptet. Strikte Beweise hierfür sind jedoch meines Wissens bisher noch nicht erbracht worden. Ragg<sup>1</sup> hat zwar zwischen mit Farben bemalten Glasplatten und Eisen Ströme nachgewiesen und empfiehlt auch einen solchen Nachweis ganz allgemein für die Güte von Anstrichen. Die Farben, mit denen er diese Versuche ausführte, enthielten jedoch alle metallischen Zinkstaub; ob der von ihm vorgeschlagene Versuch bei gewöhnlichen Farben messbare Ströme giebt, erscheint, nach in derselben Weise von Herrn Spitzer und mir angestellten resultatlosen Versuchen

<sup>1</sup>M. Ragg Jahrbuch der Schiffbautechn. Ges. Berlin 6, 389 (1905)

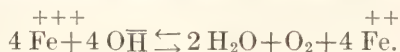
zweifelhaft. Dieser negative Ausfall beweist aber nichts gegen das Bestehen von Potentialdifferenzen zwischen Farben und Eisen, da alle Versuche, um Ströme zu messen, bei der Kleinheit der in Frage kommenden Potentialdifferenzen und der Grösse des Widerstandes der Farbe bei einer derartigen Versuchsanordnung, zu keinem Resultate führen dürften.

Der Nachweis der gesuchten Potentialdifferenzen ist eben nur mit einem empfindlichen Electrometer möglich.

Es lag mir daran zuerst festzustellen, ob einer der gebräuchlichen Farbkörper ohne Leinöl gegen Eisen oder gegen die Hg-HgCl Normalelectrode Potentialdifferenzen aufweist. Ich wählte hierzu anfangs Eisenoxyd ( $\text{Fe}_2\text{O}_3$ ) später auch noch Zinkoxyd ( $\text{ZnO}$ ) Bleicarbonat ( $\text{PbCO}_3$ ) und Bleimennige ( $\text{Pb}_3\text{O}_4$ ).

Die Herstellung von Electroden aus diesen Substanzen wurde in liebenswürdiger Weise von Herrn Wünsch mit einer eisernen cylindrischen Presse ausgeführt. Die in Stangenform gepressten Stücke hatten einen Durchmesser von 1 cm. und eine Länge von ungefähr 3-4 cm. Die Messungen wurden mit dem vorher erwähnten Electrometer und einem Compensationsapparat von Siemens & Halske nach der Compensationsmethode in bekannter Weise ausgeführt. Der Electrolyt, in den die Electrode tauchte —wieder neutrale 1-10 n-KCl-Lösung—enthielt  $\text{Fe}_2\text{O}_3$  als Bodenkörper, nachdem er hiermit ordentlich durchgeschüttelt worden war. Die Lösung wurde später zuerst mit NaOH schwach alkalisch und nachher mit  $\text{H}_2\text{SO}_4$  schwach sauer gemacht. Als gegenelectroden wurden die Hg-HgCl-Normalelectrode oder Eisenelectroden benutzt.

In der neutralen und schwach alkalischen Lösung waren die gemessenen Potentialdifferenzen äusserst inconstant, sie wurden ständig kleiner. Als Grund hierfür ist es möglich anzunehmen, dass die OH-Jonen Concentration infolge des sich an der  $\text{Fe}_2\text{O}_3$ -Electrode abspielenden Vorganges, stetig geringer wird. Es ist nämlich wahrscheinlich, dass dieser Vorgang folgender ist:



Es spricht auch hierfür, dass in saurer Lösung die Potentialwerte gegen die Normalelectrode absolut constant wurden und sich jederzeit reproduzieren liessen.

Die Resultate waren im Einzelnen folgende:

A.  $\text{Fe}_2\text{O}_3$ —Electrode in neutraler Lösung

$$\text{Fe}_2\text{O}_3 \left| \text{KCl} \right| \text{KCl} \left| \text{Hg} \right| 20^\circ \left| \begin{array}{c} -0,37 \text{ Volt} \\ \text{bis} \\ -0,25 \text{ Volt} \end{array} \right| \begin{array}{c} E_h = -0,03 \\ \text{bis} \\ +0,09 \end{array} \left| \begin{array}{c} \text{ungenau} \\ \\ \end{array} \right|$$

d.h.:  $\text{Fe}_2\text{O}_3$  ist um ca. 0,3 Volt unedler oder zinkischer als Hg.

Anmkg.: Um die Werte auf die Wasserstoff Normal-Electrode  $E_h$  zu beziehen, sind den gefunden Werten +0,337 Volt zuzuzählen.

B.  $\text{Fe}_2\text{O}_3$ —Electrode in schwach alkalischer Lösung (1 cm.<sup>3</sup> 40% NaOH auf 1,5 l. neutraler 1-10 n-KCl Lösung)

$$\text{Fe}_2\text{O}_3 \left| \text{KCl NaOH} \right| \text{KCl} \left| \text{Hg} \right| 20^\circ \left| \begin{array}{c} -0,55 \text{ Volt} \\ \text{bis} \\ -0,49 \text{ Volt} \end{array} \right| \begin{array}{c} E_h = -0,21 \\ \text{bis} \\ -0,15 \end{array} \left| \begin{array}{c} \text{ungenau} \\ \\ \end{array} \right|$$

d.h.  $\text{Fe}_2\text{O}_3$  ist um ca. 0,5 Volt unedler oder zinkischer als Hg.

C.  $\text{Fe}_2\text{O}_3$ -Electrode in saurer Lösung (1 cm.<sup>3</sup> 10%  $\text{H}_2\text{SO}_4$  auf 1,5 l. neutraler 1-10 n. KCl Lösung)

$$\text{Fe}_2\text{O}_3 \left| \text{KCl, H}_2\text{SO}_4 \right| \text{KCl} \left| \text{Hg} \right| 20^\circ \left| -0,526 \text{ Volt} \right| E_h = -0,186$$

$$\text{Fe}_2\text{O}_3 \left| \text{KCl, H}_2\text{SO}_4 \right| \text{Fe (frisch)} \left| 20^\circ \right| +0,090 \text{ Volt}$$

d.h.  $\text{Fe}_2\text{O}_3$  ist um 0,526 Volt unedler oder zinkischer als Hg, aber um 0,090 Volt edler als metallisches Eisen.

D.  $\text{ZnO}$ ,  $\text{PbCo}_3$ ,  $\text{Pb}_3\text{O}_4$  in saurer Lösung

$$\begin{array}{l} \text{ZnO KCl, H}_2\text{SO}_4 \text{ Fe (frisch) } 20^\circ +0,150 \text{ Volt} \\ \text{PbCo}_3 \text{ KCl, H}_2\text{SO}_4 \text{ Fe ( " ) } 20^\circ +0,095 \text{ " } \\ \text{Pb}_3\text{O}_4 \text{ KCl, H}_2\text{SO}_4 \text{ Fe ( " ) } 20^\circ +0,075 \text{ " } \\ \text{Fe}_2\text{O}_3 \text{ KCl, H}_2\text{SO}_4 \text{ Fe ( " ) } 20^\circ +0,090 \text{ " } \end{array}$$

Die Werte für Eisen mit Hammerschlag sind stets um ungef. 0,02 bis 0,04 Volt grösser.

Die Farbkörper sind also alle um gegen 0,1 Volt edler als Eisen. Dies erscheint im ersten Augenblick überraschend. Die Erklär-



ung mag aber die sein, dass die Farbkörper sehr wenig positive Ionen (oder vielleicht sogar negative Ionen) in Lösung senden.

Es ist also hiermit nachgewiesen, dass die gebräuchlichsten Farbkörper an sich Potentialdifferenzen gegen das Eisen aufweisen, die zu ungunsten des Eisens ausfallen. Es fragt sich nun nur noch, ob das Leinöl die Farbpartikel nicht bei Anstrichen vollkommen umhüllt, so dass es in Praxi zu Potentialdifferenzen nicht kommen kann. Dass dem nicht so ist, hat seiner Zeit Herr Ragg,<sup>1</sup> durch die weiter oben geschilderten Versuche schon nachgewiesen, und auch Herr Kröhnke<sup>2</sup> berichtet, dass man bei Anstrichen mit Zinkstaub, die sich in schwach mit Salpetersäure angesäuerter Lösung befinden, nach einiger Zeit chemisch Zink in dieser Lösung nachweisen kann.

Um auch diese Frage nochmals nachzuprüfen, versuchte ich eine mit Eisenoxyd-Leinölfarbe bestrichene und über einen Monat getrocknete Glasplatte mit dem Compensationsapparat und Electrometer gegen die Normal-Electrode zu messen. Als Electrolyt nahm ich wieder die schwach saure 1-10 n-KCl Lösung. Der Widerstand der Farbe zwischen dem Electrolyten und der Klemmschraube erwies sich aber zu gross, um nach der Compensationsmethode zu Resultaten zu gelangen; er wirkte wie eine Stromunterbrechung. Ich griff darauf auf das einfache Verfahren zurück die zu suchende Spannung direkt an das Electrometer anzulagen. Dies führte zu einem Resultat. Der erste Ausschlag war, wie bei den Messungen mit Leinölfirnis ein verhältnissmässig grosser; er entsprach einer Potentialdifferenz von ungef.  $-0,78$  Volt, (das Vorzeichen auf die Farbe bezogen). Alsdann stellte sich das Electrometer ziemlich constant auf ungef.  $-10,0$  cm ein. Dies entspricht einer Potentialdifferenz von  $-0,57$  Volt. Dies wäre ungefähr die Potentialdifferenz  $= (-0,55V)$ , die  $Fe_2O_3$  allein in saurer Lösung gegen die Normalelectrode zeigte. Hiermit scheint der Nachweis erbracht zu sein, dass, wenn auch die Verhältnisse an einer Farben-Electrode ziemlich undefiniert sind, es doch im Wesentlichen auf die Farbkörper oder allgemein gesagt, auf die im Leinöl eingebetteten Substanzen ankommt.

<sup>1</sup> M. Ragg l. c.

<sup>2</sup> O. Kröhnke, üb. Schutzanstriche eis. Röhren Leipzig 1910.



Es wäre allerdings nun noch möglich, dass die zwischen Farbkörper und Eisen bestehenden Potentialdifferenzen es zu einer Electrolyse nicht kommen lassen können, weil der electriche Widerstand der Farbkörper zu gross wäre. Ich habe aber schon kürzlich<sup>1</sup> darauf hingewiesen, dass, wenn auch der spec. Widerstand einer gerade trocken gewordenen Eisenoxyd-Leinölfarbe ungef. 5. 106 beträgt, der tatsächliche in Frage kommende Widerstand doch nur verhältnissmässig gering ausfallen wird, da er sich nur auf nach 1-100 mm zählenden Strecken mit beliebig grossem Querschnitt geltend macht. Auch nimmt ja, wie Cushman u. Gardner<sup>2</sup> zeigten die Leitfähigkeit mit dem Feuchtigkeitsgrad der Farben ungeheuer zu. Ein derartiger Einwand ist also nicht zu fürchten und dem Eintreten der Electrolyse steht nichts im Wege.

Wie Herr Spitzer und ich zu zeigen Gelegenheit hatten,<sup>3</sup> nimmt das Rosten von Eisen unter Anstrichen mit zunehmender Anzahl der Anstriche zu. Diese auffallende Tatsache scheint uns darauf hinzudeuten, dass electrochemische Prozesse hier vor sich gehen müssen, die eine eingehende Untersuchung verlangen. Es war uns jedoch bisher nicht gewiss, ob man tatsächlich die Berechtigung hat solche annehmen zu dürfen. Die vorliegenden Untersuchungen stellen somit einen Schritt zu Klärung dieser Erscheinungen dar. Die weiteren in dieser Hinsicht angestellten Untersuchungen werden wir an anderer Stelle Gelegenheit haben zur Discussion zu stellen.

Wie ich ausgeführt habe, liegen die Verhältnisse bei Anstrichen so, dass der eingebettete Farbkörper eine wesentliche Rolle spielt. Es wird daher auf seine Auswahl zweckmässig grosse Sorgfalt zu legen sein. In erster Linie werden indess dabei seine maler-technischen Eigenschaften, insbesondere Weichheit, Deckvermögen und Haltbarkeit zu berücksichtigen sein, und hier wird man wohl von den gebräuchlichen Körpern Zinkoxyd, Eisenoxyd, Bleiweiss und Mennige kaum abgehen können. Man wird jedoch—und dies geschieht auch tatsächlich schon—den Farb-

<sup>1</sup>E. Liebreich u. F. Spitzer l. c.

<sup>2</sup>Cushman u. Gardner. *The Corrosion & Preservation of Iron & Steel* 1910 p. 170.

<sup>3</sup>l. c.

körpern Zusätze geben können, welche das Potential des Eisens günstig beeinflussen.

Den ersten Schritt auf diesem Wege hat man mit dem Zusatz von metallischem Zink-oder Aluminium-Staub gemacht. Theoretisch ist dieses Vorgehen absolut richtig; doch vermögen diese Farben, da die schützende Reichweite dieser Partikel recht gering ist und sie ausserdem, da die Leinölschicht von den Teilchen durchbohrt wird und Feuchtigkeit kapillar in diese kleinen Verletzungen eindringt, keinen effectiven Rostschutz zu gewähren, wie man sich leicht überzeugen kann, wenn man derartige Anstriche in Wasserdampf während 1 bis 2 Tagen längen lässt.

In verbessernder Weise hat man diesen Weg in Amerika und Deutschland jedoch weiter verfolgt.

In Amerika sind es die Farben mit Zusätzen von gewissen Chromsalzen, welche zuerst Wood<sup>1</sup> vorgeschlagen hat. Derartige Farben sind dann von verschiedenen, insbesondere von Cushman und Gardner geprüft und empfohlen worden. Die durch die eindringende Feuchtigkeit sich etwas lösenden Chromsalze passiviren das Eisen und wirken auf diese Weise rostschützend. Es ist nur zu bedauern, dass die geeigneten dieser Salze, dadurch dass sie wie Cushman und Gardner angeben, das Trocknen des Oeles bedeutend erschweren und auch wohl verhältnissmässig sehr teuer sind, in ihrem Wert herabgemindert werden.

Diese beiden Gründe machen es leider nicht möglich diese ausgezeichneten Rostschutzmittel in dem Procentsatz der Farbe beizumengen, der nötig ist, damit seine panivierenden Eigenschaften in vollem Umfange zur Geltung kommen können; immerhin wird auf diesem Wege des Passivierens noch mancher Fortschritt zu erreichen sein.

Der in Deutschland eingeschlagene Weg ähnelt dem in Amerika eingeschlagenen. Hier wird die Eigenschaft des Eisens benutzt in nicht concentrirten alkalischen Lösungen ein verhältnissmässig edles Potential anzunehmen. Diese Verhältnisse sind von Mugdan<sup>2</sup> genau untersucht worden.

Nach diesem Beobachter liegt die von ihm ausgesprochene

<sup>1</sup>Wood, Am. Soc. Mech. Eng. Trans. 1895, 16, 671.

<sup>2</sup>M. Mugdan, Zeitschrift, f. Electrochemie 1903, p. 442.

Vermutung nahe, dass das in  $\text{Na}_2\text{SO}_4$  gemessene Wasserstoff Potential von  $-0,25$  Volt (gegen die H—H-Normalelectrode gemessen) denjenigen Wert angiebt, welcher die die Rostung beschleunigenden und verhindernden Lösungen trennt, woraus folgen würde, dass die Bedingung des Eisenangriffes primär wasserzeretzung wäre. Dies stimmt mit seinen Beobachtungen überein. Es würde demnach praktisch darauf ankommen das Eisen mit solchen Lösungen zu umgeben, in denen es gegen die Wasserstoffnormalelectrode einen edleren Wert als  $-0,25$  Volt zeigt. Da das H-Potential in alkalischer Lösung noch unedler wird, ( $-0,74$ ) so ist eine Rostgefahr für das Eisen in alkalischen Lösungen mittlerer Concentration nicht vorhanden, in denen es Potentiale von  $+0,06$  Volt (in z. B.  $0,05$  n-NaOH) annimmt. Erst in ganz concentrischen Laugen zeigt es wieder ein wesentlich unedleres Potential ( $-0,88$  Volt), so dass Icht die Bedingungen eines Angriffes wieder gegeben sind, was auch mit den Tatsachen übereinstimmt.

Ich hatte Gelegenheit mich mit der rostschtützenden Wirkung von Farben mit Zusätzen solcher Art zu befassen, wobei sich insbesondere diejenigen Alkaliverbindungen als geeignet zeigten, welche bei Zutritt von Wasser direct NaOH oder KoH abspalten. Es sind dies besonders die Amide der Alkali-Gruppe. Vergleichende Rostungsversuche zeigten, dass Farben mit diesen Zusätzen eine unvergleichlich höhere rostschtützende Wirkung zukam, als allen denjenigen deutschen Handels-Farben, welche ich zu untersuchen Gelegenheit hatte. Derartige Farben<sup>1</sup> zeigten aber zuerst den Uebelstand, dass sie sich verseigten und es bedurfte erst längerer Untersuchungen, um dieses Uebelstandes Herr zu werden; nach Ueberwindung dieser Schwierigkeiten scheinen mir insbesondere die erwähnten alkalischen Zusätze ein vorzügliches Mittel zu sein, um das Rosten unter den Anstrichen zu verhindern, wie sich dies auch aus praktischen Versuchen ergeben hat.

Die in dieser Arbeit mitgetheilten Potentialmessungen wurden mit den Mitteln des physikalisch-chemischen Instituts der tech-

<sup>1</sup>Diese nach mir benannten Farben werden von den ebenfalls nach mir benannten Rostschutz-Farbwerken in Reinickendorf bei Berlin hergestellt, welche ausschliesslich derartige Farben fabrizieren.

nischen Hochschule zu Danzig ausgeführt, die mir Herr Professor F. Krüger in liebenswürdigster Weise zur Verfügung stellte. Ich möchte Herrn Professor Krüger an dieser Stelle meinen ganz besonderen Dank hierfür aussprechen. Die übrigen erwähnten Untersuchungen führte ich im Wesentlichen der technischen Mittelschule der Stadt Berlin zusammen mit Herrn Dr. F. Spitzer aus, welchem ich ebenfalls meinen Dank für seine Mitarbeit auszusprechen gerne Gelegenheit nehme.

## HERRING OIL

ABRAHAM LUSSKIN

*New York City*

Within recent years the subject of fish oils has received considerable attention first from the leather and soap manufacturers and subsequently from the paint chemist. Hitherto fish oil played the role of a rather unimportant by-product in the course of fertilizer or "scrap" production, for which there seems to have been always a large demand.

As the peculiar properties and industrial possibilities of fish oils became more thoroughly appreciated in the light of investigations carried out by progressive manufacturers, the fish oil industry received a new lease of life and grew until it rivalled in importance the fertilizer industry to which it had previously been a tributary.

Of all the numerous varieties of fish oils which have at one time or another appeared upon the market, Menhaden Oil alone seems to have established itself on a firm basis in the manufacture of special kinds of heat-resisting paints. Its application, therefore, is no longer an experiment; it is an established fact.

Latterly, attention has been more particularly directed toward seal, whale, cod, porpoise, and herring oils, with a view to investigating their utilizability in the industries. Of these, seal, cod and porpoise body oils have proved to be in many ways as good as menhaden oil, but are beyond the reach of the paint manufacturer on account of considerations of price.

Whale oil, which is now obtainable in the form of a clear, pale material, comparatively free from objectionable odors, has not as yet been successfully manipulated to give very good drying results.

In the treatment of fish oils, several considerations must be constantly kept in mind in order to obtain the best results:

1. The oil must be free from high melting point glycerides or fatty acids; or, to use the technical term, the oil must be "winter pressed." Most fish oils contain a large amount of saturated glycerides of the nature of palmatin which separate from the



oils on standing for any length of time at a low temperature. When these have been removed from the oil, the resulting product is found to be much more amenable to successful treatment than it otherwise is. It would seem that these high melting point fats tend to retard or to prevent the drying of fish oils, giving films which remain greasy for a very long time.

2. Very frequently, oils are received which have a high content of free fatty acids. In the case of one sample of herring oil, this was as high as 41.9. Under such circumstances, it is perfectly evident that the drying of the oil would be very largely inhibited. In addition, such an oil, used as a paint vehicle, in conjunction with pigments like red lead, white lead, and zinc oxide will, in a very short space of time, "liver" up and form the lead and zinc soaps of the fatty acids. This was very largely responsible for the poor results obtained with the fish oils which were first introduced on the market. The free fatty acids are formed when the oil, extracted from the fish by boiling in water, is subjected to the action of the decomposition products from the bodies of the fish for a longer time than is absolutely necessary to break open the oil-containing cells.

3. Finally it must be remembered that driers, which serve very well for vegetable drying oils, will not, in general, function properly, when utilized for fish oils. The tungate driers, and particularly the Cobalt tungates, can generally be depended upon in the case of oils which do not yield to the action of the ordinary linseed oil driers, provided, however, the two conditions named above have been satisfied.

The writer recently had his attention called to several grades of herring oil, which, at first glance, appeared desirable from the paint manufacturer's standpoint. Accordingly an investigation was started to test its adaptability for paint purposes, and to compare its behavior with that of Menhaden oil.

Herring oil occurs in the bodies of *Clupeus C.* and *V.* (Japanese herring varieties) and *Clupeus harengus* (European or North Sea herring).

The plan of extracting the oil from herring is the one which is universally used in the fish oil industry, viz., extraction in boiling water.

Two representative samples of herring oil, furnished by two of the leading oil concerns in the States, were experimented with in conjunction with menhaden and other fish oils. The following analytical constants were obtained:

| No.                                   | Color             | Odor           | Sp. Gr.<br>15° C | Acid<br>Value | Iodine<br>Value |
|---------------------------------------|-------------------|----------------|------------------|---------------|-----------------|
| #1 Herring Oil                        | Very Pale         | Good           | 0.9240           | 2.4           | 137.9           |
| #2 Herring Oil                        | Dark Brown        | Bad            | 0.9210           | 41.9          | 136.1           |
| Blown Oil #2                          | Deep Red          | Almost<br>None | 0.9654           | 25.7          | 89.94           |
| Winter-Pressed }<br>Refined } #2<br>* | Extremely<br>Pale | Fair           | 0.920            | 39.4          | 136.1           |
| #1 Crude Whale Oil                    | Very Pale         | Good           | 0.9230           | 0.6           | 136.1           |
| #1 Filt. Whale Oil                    | Very Pale         | Good           | 0.9203           | 2.3           | 125.0           |
| #2 Filt. Whale Oil                    | Pale Amber        | Very good      | 0.9222           | 14.5          | 142.9           |
| Porpoise Body Oil                     | Very Pale         | Very good      | 0.9268           | 2.8           | 132.3           |
| Menhaden Oils                         |                   |                |                  |               |                 |
| Ext. Bleached Winter<br>Oil           | Very Pale         | Fair           | 0.9272           | 0.5           | 150.4           |
| Bleached-Refined                      | Pale Amber        | Not Bad        | 0.9308           | 5.7           | 161.2           |
| Regular                               | Deep Red          | Bad            | 0.9284           | 8.4           | 165.7           |

Crude herring oil, even though very dark in color, yields a very clear, pale product when treated with Fuller's earth for a short time at about 250° F., and then for some time longer, at the temperature of boiling water. In addition the odor is considerably improved.

In the case of the crude herring oil listed above, the sample was kept for several hours at about 60 F. to permit high-melting fats to separate out. The portion which remained liquid corresponded to a winter-pressed oil. Since the acid and iodine numbers were practically unchanged it seems that the solid fats

\*The part of the table below the asterisk (with exception of the acid values), is from a paper on Fish Oils delivered by Mr. M. Toch before the Amer. Chem. Soc. Dec. 1911 and published in the Journal of Industrial and Engineering Chemistry.

contained saturated and unsaturated compounds in about the same proportion as the crude oil.

Another sample of the oil was heated to 320° F. and blown with air for about 8 hours. The effect produced on the constants are shown above. The oil was very heavy and viscous but had the deep red color which fish oils so readily assume. It must be noted also that the "fishy" odor was very faint. The reduction in acid value would seem to indicate that the oil contained fatty acids which were volatile at the temperature of blowing.

Attempts to dry the samples of herring oil did not prove successful, even when very powerful driers were used. This cannot, however, be interpreted to mean that herring oils are, in general, not capable of drying.

Porpoise body oil and menhaden oil, under similar conditions, dried satisfactorily.

The blown herring oil could very well be used for the production of smoke-stack paints, and for paints intended to resist the "Chalking" action of salt air. Herring oil is at present used to a certain extent in leather manufacture together with some of the other fish oils like menhaden and whale oil. In regard to herring oil, as with many of the other materials which are being introduced from time to time, the final word cannot be spoken until many more specimens have been examined and given a fair test.

# MOISTURE AND THE DRYING OF THE LINSEED OIL FILM

HANS MANNHARDT

*Heath & Milligan Mfg. Co., Chicago, Ill.*

It is a well known fact that a linseed oil film does not dry properly in damp weather. The subject has been discussed by a number of investigators and as their experimental modes of procedure have differed, their conclusions have been somewhat at variance. It is believed that the apparatus employed in this experiment differs from those of previous experimenters.

|  |   |                 |
|--|---|-----------------|
| Compressed air tap                               | } | Purifying train |
| 2 liter water trap                               |   |                 |
| 2 liter bottle containing concentrated $H_2SO_4$ |   |                 |
| Safety bottle                                    |   |                 |
| Wash bottle, 100 cc 50% Na OH                    |   |                 |
| $CaCl_2$ bottle 100 g NaOH. $Ca(OH)_2$           |   |                 |
| Safety bottle                                    |   |                 |
| Wash bottle, 100 cc conc. $H_2SO_4$              |   |                 |
| 2 Mohr bulbs, conc. $H_2SO_4$                    |   |                 |

|                 |   |                               |   |           |
|-----------------|---|-------------------------------|---|-----------|
| $CaCl_2$ bottle | { | 300 grams silica flour and    | } | Reaction  |
| charged with    | { | 30 grams "boiled" linseed oil | } | Bottle #1 |

|  |   |                     |
|--|---|---------------------|
| Mohr bulb, conc. $H_2SO_4$               | } | Absorption train #1 |
| Mohr bulb, conc. $H_2SO_4$               |   |                     |
| 20 cm. straight—one bulb tube, soda lime |   |                     |
| U-tube, pumice and $H_2SO_4$             |   |                     |

|  |                     |
|--|---------------------|
| Reaction Bottle #2 like R. B. #1.....  | Reaction Bottle #2  |
| Absorption train #2 like A. T. #1..... | Absorption train #2 |

|  |             |
|--|-------------|
| 3 Bulb—U-tube—conc. $H_2SO_4$ .....        | Safety tube |
| $3\frac{1}{2}$ liter aspirator bottle..... | Suction     |

Necessary stoppers were of sound cork thoroughly soaked with paraffine wax at 100° C. and sealed in place with paraffine wax. Joints between the contiguous pieces of apparatus were made with fresh pure gum-tubing wired in place and blank experiments were made to ascertain the efficiency of the purifying train and various joints.

*The object* of this train of apparatus was to establish whether conc.  $\text{H}_2\text{SO}_4$  and soda-lime could retain those products of linseed oil which retard its drying.

*The oil used*, when one gram was spread uniformly through ten grams of silica flour, gained 16% in weight in 18 hours at 20°C.

Usually about seven liters of *purified air* passed through the apparatus in the course of an eight-hour day. The apparatus remained idle on Saturdays and Sundays.

*Organic volatile.* The sulphuric acid in each of the Mohr bulbs immediately following the reaction jars, was colored to about the color and depth of a tenth-normal iodine solution. The next Mohr bulb contents were not colored.

*Observations.* The first Mohr bulbs of the two absorption trains apparently absorbed all the " $\text{H}_2\text{O}$ , etc.," and the small gains in weight of the next Mohr bulbs was considered as being derived from the soda-limes following and therefore added to the gains in weight due to " $\text{CO}_2$ , etc."

The following weighings were taken:

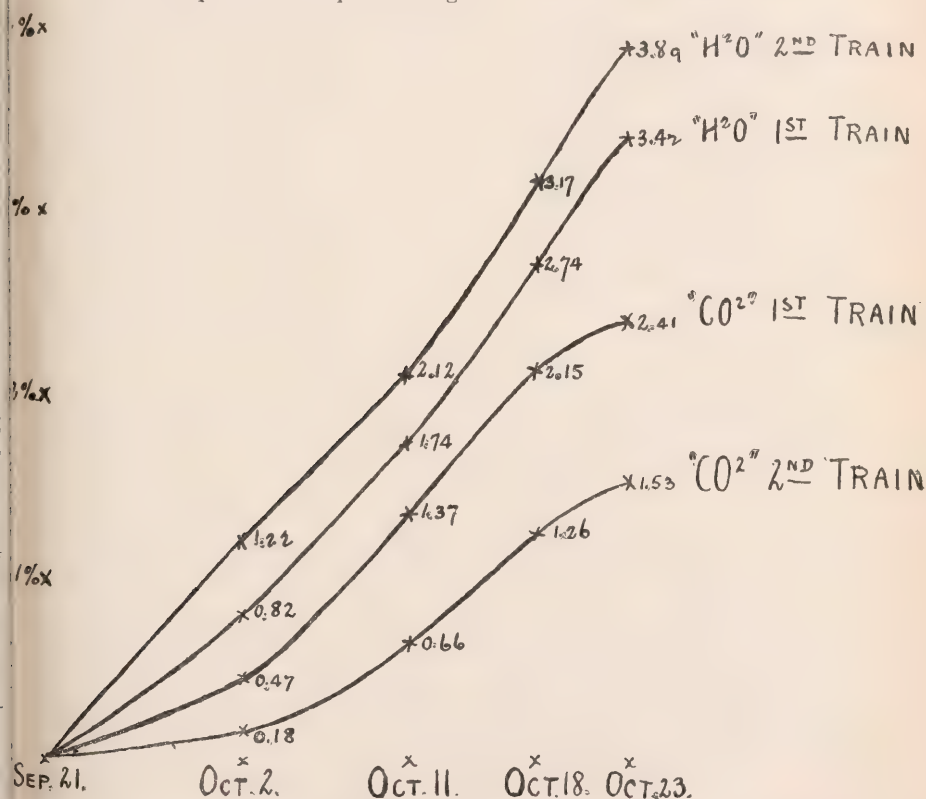
| Increments<br>" $\text{H}_2\text{O}$ etc." | Train #1       | Increments " $\text{CO}_2$ etc." |   |                         |   |
|--|----------------|----------------------------------|---|-------------------------|---|
|  |                | $\text{H}_2\text{SO}_4$          | $\text{NaOH}$ .<br>$\text{Ca}(\text{OH})_2$ | $\text{H}_2\text{SO}_4$ |   |
| 0.245                                      | 9-21 to 10-2   | .003                             | .097  | .042                    | Column of<br>silica and oil<br>about six<br>inches deep |
| 0.276                                      | 10-2 to 10-11  | .000                             | .229  | .040                    |   |
| 0.299                                      | 10-11 to 10-18 | .000                             | .202  | .032                    |   |
| 0.205                                      | 10-18 to 10-23 | .000                             | .052  | .027                    |   |
| 1.025                                      |                |                                  |   | 0.724                   |   |

" $\text{H}_2\text{O}$ " plus " $\text{CO}_2$ " equals 1.749 g.



|       | Train #2       |      |      |       |                                      |
|-------|----------------|------|------|-------|--------------------------------------|
| 0.366 | 9-21 to 10-2   | .002 | .017 | .034  | Column about<br>eight inches<br>deep |
| 0.270 | 10-2 to 10-11  | .001 | .113 | .030  |                                      |
| 0.315 | 10-11 to 10-18 | .000 | .150 | .031  |                                      |
| 0.215 | 10-18 to 10-23 | .001 | .059 | .022  |                                      |
| 1.166 |                |      |      | 0.460 |                                      |

"H<sub>2</sub>O" plus "CO<sub>2</sub>" equals 1.626 g.



While these curves show that the oxidation was by no means completed, the two Ca Cl<sub>2</sub> jars were opened at the end of the experiment and 10.000 grams at once weighed out from the top and from the bottom of each jar and placed in shallow dishes.

|         |         | Top #1  | Bottom #1                                     | Top #2  | Bottom #2                                     |
|---------|---------|---|---|---|---|
| 4 P. M. | Oct. 23 | 19.040  | 19.720  | 21.800  | 19.030  |
| 5 P. M. | Oct. 23 | 19.030  | 19.713  | 21.790  | 19.025  |
| 9 A. M. | Oct. 24 | 19.010  | 19.702  | 21.769  | 19.005  |
| 9 A. M. | Oct. 25 | 19.907  | 19.687  | 21.764  | 19.002  |
| 9 A. M. | Oct. 30 | 19.002  | 19.084  | 21.764  | 19.002  |
| 9 A. M. | Oct. 30 | placed over<br>H <sub>2</sub> SO <sub>4</sub> | placed over<br>H <sub>2</sub> SO <sub>4</sub> | placed over<br>H <sub>2</sub> SO <sub>4</sub> | placed over<br>H <sub>2</sub> SO <sub>4</sub> |
| 5 P. M. | Nov. 2  | 19.893  | 19.660  | 21.755  | 18.990  |
| 5 P. M. | Nov. 2  | placed over<br>H <sub>2</sub> SO <sub>4</sub> | returned to<br>room air                       | placed over<br>H <sub>2</sub> SO <sub>4</sub> | returned to<br>room air                       |
|         |         | 19.897  | 19.680  | 21.757  | 18.997  |
| 3 P. M. | Nov. 6  | 19.002  | 19.684  | 21.762  | 19.002  |
| 12 M.   | Nov. 28 | 19.004  | 19.084  | 21.763  | 19.004  |
|         |         |   |   |   | Foggy weather                                 |
| 12 M.   | Nov. 28 | in air  | placed over<br>H <sub>2</sub> SO <sub>4</sub> | in air  | placed over<br>H <sub>2</sub> SO <sub>4</sub> |
| 8 A. M. | Nov. 29 | 19.903  | 19.673  | 21.762  | 18.993  |

In the five weeks between Oct. 23 and Nov. 28 we have—

|  |        |        |        |        |
|--|--------|--------|--------|--------|
|  | —0.000 | —0.066 | —0.067 | —0.026 |
|--|--------|--------|--------|--------|

which referred to about 0.000 g. original oil is an average loss of about 4.7%.

Approximately 161 liters of air free from CO<sub>2</sub> and H<sub>2</sub>O were passed through the double train during the first half of the experiment. The results show that during the 21 days during which the air was passed and the intermediate Saturdays and Sundays of rest, the linseed oil gave up:

in CaCl<sub>2</sub> jar #1 0.05% C., 0.38% H.

in CaCl<sub>2</sub> jar #2 0.34% C., 0.43% H.

and if the jars and contents had been weighed before and after the run we would also know whether any oxygen was given off by the oil. This could easily be done by some future investigator.

1 gram of water is sufficient to saturate—

|                                      |  |
|--------------------------------------|--|
| 108 liters of air at 10° C. 760 m.m. | } Meyers Groses Konvers,<br>Lexikon, "Luft feuchtig-<br>keit" s. 809 |
| 58 " " " " 20° C. 760 m.m.           |  |
| 33 " " " " 30° C. 760 m.m.           |  |

As the laboratory temperature averaged 20° C. with little variation during this experiment, the air coming off the reaction jars was about one-third saturated with moisture, a low humidity, very favorable for the drying of linseed oil.

The actual drying or setting of the linseed oil must have taken place on September 21st and 22nd, each reaction jar consuming about 5 grams or 3½ liters of oxygen, though no measurements were made of this presumptive state of affairs.

The curves for H<sub>2</sub>O given off are almost linear and show no tendency toward the horizontal at the 23rd of October. The further loss in weight of about 4% which the linoxyn underwent from October 23rd to November 29th was presumably largely made up of H<sub>2</sub>O.

It is possible that the drying consists of:

|                          |  |
|--------------------------|--|
| PERIOD "A"<br>9-21-10-2  | { Fixation of oxygen, little decarbonization, some dehydrogenization, about 49 liters of air were passed into the apparatus; 36 liters of air may be sufficient to dry the oil |
| PERIOD "B"<br>10-2-10-18 | { Main period of decarbonization<br>Some dehydrogenization   |
| PERIOD "C"<br>10-18—     | { Dehydrogenization chiefly  |

If the reaction jars had been weighed and the other determinations had been made at more frequent intervals the process would have given a further insight into the mechanism of the drying of linseed oil.

Presumably, combustion determinations of the carbon and the hydrogen in linoxyn have been made with the air-dry product and this certainly is open to some criticism owing to the moderate hygroscopicity of the linoxyn.



## THE DECOMPOSITION OF LINSEED OIL DURING DRYING

J. C. OLSEN AND A. E. RATNER  
*Polytechnic Institute, Brooklyn, N. Y.*

There are various statements in the literature on linseed oil that during the process of drying carbon dioxide is given off. The authors have failed to find the record of any definite experiment indicating the amount of this constituent which is evolved during the drying process. No definite information could be found with reference to the amount of water evolved. Experiments have been conducted to ascertain the increase in weight of linseed oil during drying, the assumption being that this increase in weight is due to the absorption of oxygen. It is evident that if volatile constituents are given off during the drying process, the increase in weight will not give a true measure of the oxygen absorbed.

In order to secure more definite information with reference to this very interesting and important reaction, an experiment was carried out in which pure, dry air was conducted over a weighed amount of linseed oil. The increase in weight of the linseed oil was ascertained and the moisture and carbon dioxide given off was absorbed and weighed so that the total amount of oxygen which combined with the linseed oil could be calculated.

The linseed oil used for this purpose was a sample of the oil prepared under the direction of Committee E of the Society of Testing Materials. Four samples were prepared under the direction of this committee under conditions which seem to absolutely guarantee that the samples taken are pure linseed oil. Four samples were received from Mr. G. W. Thompson, sealed and packed exactly as they were sent out by this committee for analysis.

The full description of the method of preparing these samples, as well as the analysis, may be found in the report of Committee



D of the Society of Testing Materials. The sample upon which our experiment was conducted was pressed from the seed by the National Lead Company April 1909. On the 25th of April when our experiment was begun, the oil was clear but there was a slight sediment in the bottle. The bottle was thoroughly shaken when the portion experimented on was weighed out.

5.336 grams of the linseed oil was transferred to a weighed Florence flask of 400 cc. capacity. In order to expose this large amount of oil in a thin film to the gases of the air 3.866 grams of glass wool were placed in the bottle. By previous experiment, this amount had been found just sufficient to soak up the oil after the walls of the flask has been covered by a thin film. A similar flask was used as a counter-poise in all the weighings so as to eliminate the error due to air displacement and films of moisture on the surface of the glass.

The flask containing the linseed oil was connected up in a series of tubes as follows. A glass tube extended into the open air so as to avoid acid fumes and impurities from the laboratory air. The air was first passed through a large tower containing soda lime and caustic potash in lumps, then through a Geissler bulb containing strong caustic potash solution; then through a U tube containing concentrated sulphuric acid and glass beads. The air thus freed from carbon dioxide or other acid gases and water, passed into the flask containing the linseed oil through a tube extending to the middle of the flask. The exit tube, passing out from the upper part of the flask conducted the air into a weighed U tube containing concentrated sulphuric acid and glass beads, thence into weighed Geissler bulbs containing strong caustic potash solution; then through a weighed U tube containing concentrated sulphuric acid and glass beads, then through another sulphuric acid tube to an aspirator, holding 75 liters. This aspirator drew 7.5 liters of air through the apparatus at night and 7.5 liters during the day; the flask containing the oil, the sulphuric acid tubes and the Geissler bulb being weighed morning and evening.

Before the experiment was started, the apparatus was tested over a long period of time by drawing air through in the manner indicated, and weighing the tubes night and morning until it

was certain that all sources of error had been eliminated and that the various weighed tubes had become constant. The flask designed for the linseed oil then received its charge of weighed linseed oil, and the experiment continued for 74 days. The results of the experiment are given in tabular form.

The determinations bracketed are doubtful on account of slight errors such as spattering of the liquid in the tubes, etc. Table II was calculated from Table I by adding together the daily increases in weight, so that the figures given for each day give the total quantity on that day. Table III was calculated from Table II by dividing the various quantities by the weight of oil taken, 5.366 grams.

TABLE I  
Daily Record of Weights Taken

| Days      | Increase in<br>weight of oil<br>Grams | Water given<br>off<br>Grams | Carbon Dioxide<br>given off<br>Grams |
|-----------|---------------------------------------|-----------------------------|--------------------------------------|
| 1st.....  | 0.0254                                | 0.0306                      | 0.0156                               |
| 2nd.....  | 0.0060                                | 0.0156                      | 0.0106                               |
| 3rd.....  | 0.0044                                | 0.0236                      | 0.0138                               |
| 4th.....  | 0.0060                                | 0.0316                      | 0.0244                               |
| 5th.....  | 0.0102                                | 0.0088                      | 0.0270                               |
| 6th.....  | 0.0140                                | 0.0118                      | 0.0124                               |
| 7th.....  | 0.0178                                | 0.0334                      | 0.0080                               |
| 8th.....  | 0.0286                                | 0.0164                      | 0.0038                               |
| 9th.....  | 0.0276                                | 0.0218                      | (0.0084)?                            |
| 10th..... | 0.0156                                | 0.0102                      | 0.0128                               |
| 11th..... | 0.0374                                | 0.0292                      | 0.0094                               |
| 12th..... | 0.0454                                | 0.0364                      | 0.0072                               |
| 13th..... | 0.0274                                | 0.0202                      | 0.0063                               |
| 14th..... | 0.0696                                | 0.0438                      | 0.0095                               |
| 15th..... | 0.0796                                | 0.0246                      | (0.0074)?                            |
| 16th..... | 0.0756                                | 0.0200                      | 0.0054                               |
| 17th..... | 0.0650                                | 0.0098                      | 0.0000                               |
| 18th..... | 0.0478                                | 0.0156                      | 0.0078                               |
| 19th..... | 0.0600                                | 0.0230                      | 0.0066                               |
| 20th..... | 0.0636                                | 0.0150                      | 0.0042                               |
| 21st..... | 0.0408                                | 0.0270                      | 0.0058                               |
| 22nd..... | 0.0354                                | 0.0212                      | 0.0056                               |
| 23rd..... | 0.0400                                | 0.0560                      | (0.0056)?                            |
| 24th..... | 0.0184                                | 0.0272                      | 0.0057                               |
| 25th..... | 0.0112                                | 0.0356                      | 0.0079                               |
| 27th..... | 0.0114                                | 0.0268                      | 0.0052                               |
| 28th..... | 0.0108                                | 0.0088                      | 0.0010                               |
| 30th..... | 0.0156                                | 0.0260                      | 0.0090                               |
| 32nd..... | 0.0064                                | 0.0304                      | 0.0022                               |
| 35th..... | 0.0082                                | 0.0202                      | 0.0078                               |
| 38th..... | 0.0058                                | 0.0130                      | 0.0028                               |
| 41st..... | 0.0092                                | 0.0046                      | 0.0028                               |
| 44th..... | 0.0071                                | 0.0061                      | 0.0035                               |
| 48th..... | 0.0054                                | 0.0057                      | 0.0038                               |
| 51st..... | 0.0058                                | 0.0072                      | 0.0018                               |
| 53rd..... | 0.0040                                | 0.0086                      | 0.0026                               |
| 57th..... | 0.0032                                | 0.0043                      | 0.0020                               |
| 62nd..... | 0.0012                                | 0.0068                      | 0.0025                               |
| 74th..... | 0.0011                                | 0.0052                      | 0.0007                               |

TABLE II  
Total Amount of Quantities Determined

| Days           | Increase in<br>Weight of oil<br>Grams | Water given<br>off<br>Grams | Carbon Dioxide<br>Given off<br>Grams | Total Oxygen<br>Absorbed<br>Grams |
|----------------|---------------------------------------|-----------------------------|--------------------------------------|-----------------------------------|
| 1st . . . . .  | 0.0254                                | 0.0306                      | 0.0156                               | 0.0716                            |
| 2nd . . . . .  | 0.0314                                | 0.0462                      | 0.0262                               | 0.1038                            |
| 3rd . . . . .  | 0.0358                                | 0.0698                      | 0.0400                               | 0.1456                            |
| 4th . . . . .  | 0.0418                                | 0.1014                      | 0.0644                               | 0.2076                            |
| 5th . . . . .  | 0.0520                                | 0.1102                      | 0.0914                               | 0.2536                            |
| 6th . . . . .  | 0.0660                                | 0.1220                      | 0.1038                               | 0.2918                            |
| 7th . . . . .  | 0.0838                                | 0.1554                      | 0.1118                               | 0.3510                            |
| 8th . . . . .  | 0.1124                                | 0.1718                      | 0.1156                               | 0.3998                            |
| 9th . . . . .  | 0.1400                                | 0.1936                      | 0.1240                               | 0.4576                            |
| 10th . . . . . | 0.1556                                | 0.2038                      | 0.1368                               | 0.4962                            |
| 11th . . . . . | 0.1930                                | 0.2330                      | 0.1462                               | 0.5722                            |
| 12th . . . . . | 0.2384                                | 0.2694                      | 0.1534                               | 0.6612                            |
| 13th . . . . . | 0.2658                                | 0.2896                      | 0.1597                               | 0.7151                            |
| 14th . . . . . | 0.3354                                | 0.3334                      | 0.1692                               | 0.8381                            |
| 15th . . . . . | 0.4150                                | 0.3580                      | 0.1766                               | 0.9496                            |
| 16th . . . . . | 0.4906                                | 0.3780                      | 0.1820                               | 1.0506                            |
| 17th . . . . . | 0.5556                                | 0.3878                      | 0.1820                               | 1.1254                            |
| 18th . . . . . | 0.6034                                | 0.4034                      | 0.1890                               | 1.1958                            |
| 19th . . . . . | 0.6634                                | 0.4264                      | 0.1964                               | 1.2862                            |
| 20th . . . . . | 0.7270                                | 0.4414                      | 0.2006                               | 1.3690                            |
| 21st . . . . . | 0.7678                                | 0.4684                      | 0.2064                               | 1.4426                            |
| 22nd . . . . . | 0.8032                                | 0.4896                      | 0.2120                               | 1.5048                            |
| 23rd . . . . . | 0.8432                                | 0.5456                      | 0.2176                               | 1.6064                            |
| 24th . . . . . | 0.8616                                | 0.5728                      | 0.2233                               | 1.6577                            |
| 25th . . . . . | 0.8728                                | 0.6084                      | 0.2312                               | 1.7124                            |
| 27th . . . . . | 0.8842                                | 0.6352                      | 0.2364                               | 1.7558                            |
| 28th . . . . . | 0.8950                                | 0.6440                      | 0.2374                               | 1.7764                            |
| 30th . . . . . | 0.9106                                | 0.6700                      | 0.2464                               | 1.8270                            |
| 32nd . . . . . | 0.9170                                | 0.7004                      | 0.2486                               | 1.8660                            |
| 35th . . . . . | 0.9252                                | 0.7206                      | 0.2564                               | 1.9022                            |
| 38th . . . . . | 0.9310                                | 0.7336                      | 0.2592                               | 1.9238                            |
| 41st . . . . . | 0.9402                                | 0.7382                      | 0.2620                               | 1.9404                            |
| 44th . . . . . | 0.9473                                | 0.7443                      | 0.2655                               | 1.9571                            |
| 48th . . . . . | 0.9527                                | 0.7500                      | 0.2693                               | 1.9720                            |
| 51st . . . . . | 0.9585                                | 0.7572                      | 0.2711                               | 1.9868                            |
| 53rd . . . . . | 0.9625                                | 0.7658                      | 0.2737                               | 2.0020                            |
| 57th . . . . . | 0.9657                                | 0.7701                      | 0.2757                               | 2.0115                            |
| 62nd . . . . . | 0.9669                                | 0.7769                      | 0.2782                               | 2.0220                            |
| 74th . . . . . | 0.9680                                | 0.7821                      | 0.2789                               | 2.0290                            |

TABLE III

*Total Amount of Quantities Determined in Percentage of Oil Taken*

| Days      | Increase in<br>weight of oil<br>Per cent | Water given<br>off<br>Per cent | Carbon Dioxide<br>given off<br>Per cent | Total Oxygen<br>absorbed |
|-----------|--|--------------------------------|---|--------------------------|
| 1st.....  | 0.47                                     | 0.57                           | 0.29                                    | 1.34                     |
| 2nd.....  | 0.59                                     | 0.86                           | 0.42                                    | 1.94                     |
| 3rd.....  | 0.67                                     | 1.30                           | 0.74                                    | 2.72                     |
| 4th.....  | 0.78                                     | 1.88                           | 1.20                                    | 3.97                     |
| 5th.....  | 0.97                                     | 2.06                           | 1.70                                    | 4.72                     |
| 6th.....  | 1.23                                     | 2.27                           | 1.98                                    | 5.44                     |
| 7th.....  | 1.56                                     | 2.90                           | 2.08                                    | 6.55                     |
| 8th.....  | 2.09                                     | 3.20                           | 2.16                                    | 7.45                     |
| 9th.....  | 2.61                                     | 3.61                           | 2.31                                    | 8.52                     |
| 10th..... | 2.90                                     | 3.80                           | 2.55                                    | 9.25                     |
| 11th..... | 3.60                                     | 4.34                           | 2.73                                    | 10.65                    |
| 12th..... | 4.44                                     | 5.02                           | 2.86                                    | 12.30                    |
| 13th..... | 4.76                                     | 5.40                           | 2.98                                    | 13.30                    |
| 14th..... | 6.25                                     | 6.21                           | 3.16                                    | 15.60                    |
| 15th..... | 7.73                                     | 6.67                           | 3.29                                    | 17.70                    |
| 16th..... | 9.14                                     | 7.05                           | 3.45                                    | 19.60                    |
| 17th..... | 10.35                                    | 7.21                           | 3.45                                    | 21.00                    |
| 18th..... | 11.21                                    | 7.50                           | 3.52                                    | 22.30                    |
| 19th..... | 12.31                                    | 7.84                           | 3.66                                    | 24.00                    |
| 20th..... | 13.51                                    | 8.23                           | 3.74                                    | 25.50                    |
| 21st..... | 14.30                                    | 8.72                           | 3.85                                    | 26.95                    |
| 22nd..... | 14.94                                    | 9.10                           | 3.95                                    | 28.00                    |
| 23rd..... | 15.70                                    | 10.18                          | 4.05                                    | 29.50                    |
| 24th..... | 16.00                                    | 10.67                          | 4.16                                    | 30.90                    |
| 25th..... | 16.25                                    | 11.30                          | 4.30                                    | 31.90                    |
| 27th..... | 16.41                                    | 11.80                          | 4.41                                    | 32.70                    |
| 28th..... | 16.65                                    | 12.00                          | 4.43                                    | 33.10                    |
| 30th..... | 16.95                                    | 12.50                          | 4.60                                    | 34.00                    |
| 32nd..... | 17.10                                    | 13.05                          | 4.64                                    | 34.80                    |
| 35th..... | 17.21                                    | 13.41                          | 4.78                                    | 35.50                    |
| 38th..... | 17.35                                    | 13.66                          | 4.83                                    | 35.80                    |
| 41st..... | 17.50                                    | 13.73                          | 4.89                                    | 36.20                    |
| 44th..... | 17.65                                    | 13.82                          | 4.95                                    | 36.50                    |
| 48th..... | 17.75                                    | 13.95                          | 5.03                                    | 36.80                    |
| 51st..... | 17.80                                    | 14.10                          | 5.05                                    | 37.00                    |
| 53rd..... | 17.90                                    | 14.26                          | 5.10                                    | 37.30                    |
| 57th..... | 17.95                                    | 14.35                          | 5.14                                    | 37.50                    |
| 62nd..... | 18.00                                    | 14.48                          | 5.20                                    | 37.70                    |
| 74th..... | 18.05                                    | 14.55                          | 5.21                                    | 37.80                    |



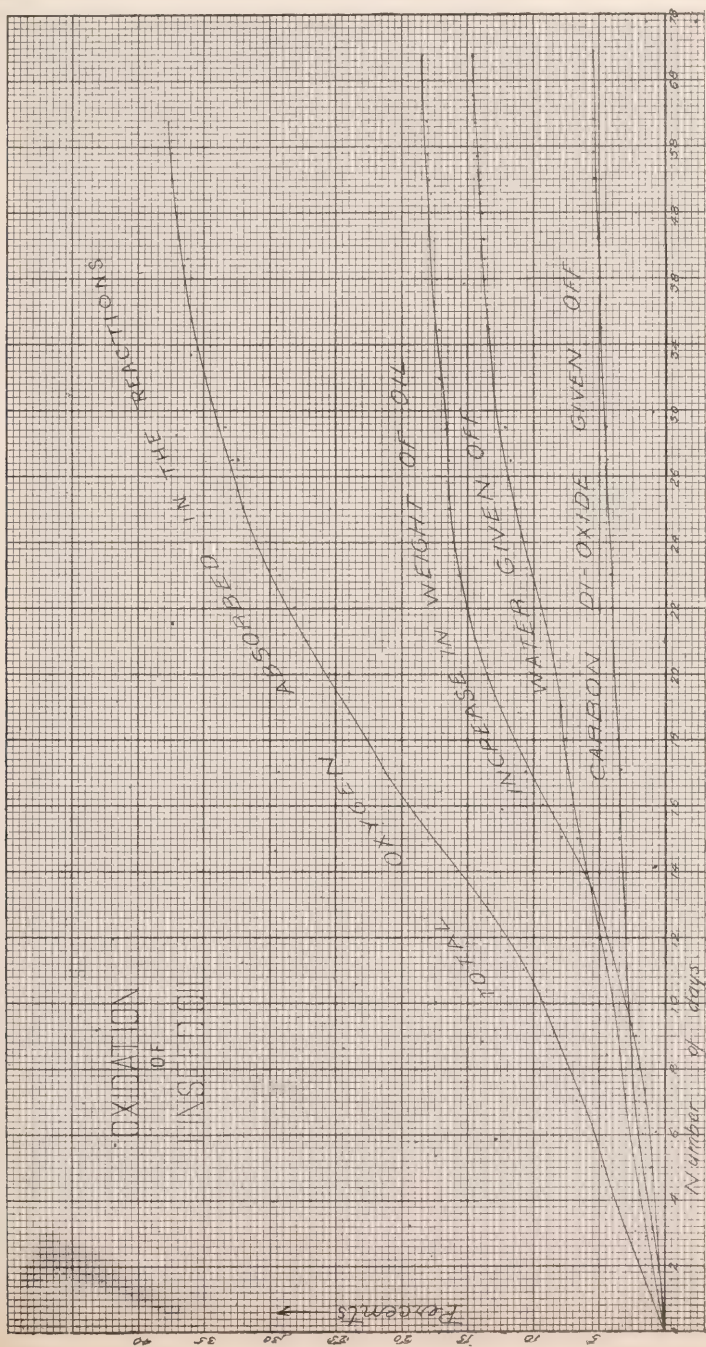
It will be noted that moisture and carbon dioxide were given off almost immediately in fairly large quantity. The oil which was slightly yellow in the beginning soon became colorless and gradually acquired a dark yellow color. Volatile matter also began to be evolved from the linseed oil. This was ascertained from the observation that small oily drops collected in the neck of the flask. The weighed sulphuric acid tube also gradually acquired a brown color which ultimately became black. This would, undoubtedly, produce an evolution of sulphur dioxide, which would be absorbed by the caustic potash solution in the Geissler bulb. Only toward the end of the experiment did the sulphuric acid tube which followed the Geissler bulb acquire a dark color. It is reasonable to suppose, therefore, that little, if any, volatile matter escaped absorption and that, therefore, while the increase in weight of the absorption tubes does not correctly represent the amount of water and carbon dioxide evolved, it does represent the total volatile matter given off by the oil, so that the increase in weight of the oil, plus the increase in weight of the absorption tubes represents the total amount of oxygen absorbed by the oil, and that experiments in which the increase in weight of the linseed oil film is noted, do not represent correctly the amount of oxygen absorbed. On the accompanying plate, a curve is drawn representing the amount of oxygen absorbed in the reaction. This was obtained from the increase in weight of the oil, plus the increase in weight of the absorption tubes. Another curve is given, showing the amount of water evolved, and another one showing the amount of carbon dioxide evolved. The accuracy of these curves and more especially the one representing the amount of water evolved, is vitiated by the fact that a volatile organic substance was produced. This volatile substance, however, is probably high in hydrogen, and an attempt will be made in the future to isolate a larger quantity of this constituent and identify it.

The composition of linseed oil is generally given as follows: Carbon 76%—Hydrogen 11%—Oxygen 13%.

Neglecting the error due to the volatile oil given off, the linseed oil lost 1.87% of its carbon and 14.73% of its hydrogen.

At the time this paper was written, the flask and the absorption tubes had not yet become constant in weight. The experiment will be continued until constant weight is obtained.

It was believed that the results, though incomplete, were of sufficient interest for publication.





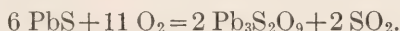
## THE MANUFACTURE AND PROPERTIES OF SUBLIMED WHITE LEAD

JOHN A. SCHAEFFER

*Picher Lead Co., Joplin, Mo.*

The manufacture of sublimed white lead, the commercial name for the basic sulphate of lead prepared by the sublimation process, depends directly upon the oxidation of galena, the sulphide of lead, when subjected to intense heat in an oxidizing atmosphere. The combustion under these conditions proceeds with violence resulting in the formation of a white sublimate, which when purified is known as sublimed white lead.

The reaction which occurs in this oxidation of galena may be written as follows:—



This formula  $\text{Pb}_3\text{S}_2\text{O}_9$  or  $2 \text{ PbSO}_4 \cdot \text{PbO}$  is analogous to the generally accepted formula for the basic carbonate of lead— $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . Commercial sublimed white lead, however, contains a higher percentage of lead sulphate than that required for the above theoretical formula. While the formation of the theoretical basic sulphate of lead is entirely feasible, its manufacture has not proven commercially advantageous. The conditions for the oxidation of the sulphide of lead are, consequently, so adjusted that a compound showing about 16 per cent. of lead oxide is obtained. The conversion of a small percentage of the lead oxide, present in the theoretical basic sulphate of lead, to lead sulphate undoubtedly results from a reaction between the lead oxide and the sulphur trioxide which forms from the oxidation of a certain amount of sulphur dioxide. A small percentage of zinc oxide is formed at the same time from the sphalerite, the sulphide of zinc, which is present in almost all non-argentiferous lead ores. It is maintained that the presence of about 6 per cent. of zinc oxide enhances the value of the pigment.



Coke, of a hard compact variety is used as fuel, while iron, in the metallic form, and limestone serve as fluxing materials together with the silica present in the ore. Any metallic lead which forms from a reduction of the lead compounds by the coke, at the intense heat continually maintained in the furnace, is separated from the readily fusible slag by a difference in their specific gravities.

Blue Fume, the fume known commercially as sublimed blue lead, is frequently added to the charge. This fume is formed in the smelting of lead ores and is recovered by the bag room process. It is found to contain about 35 per cent. of lead oxide and about 50 per cent. of lead sulphate. This fume pigment, sublimed blue lead, is rapidly finding extended use as a paint pigment for the protection of iron and steel. Its composition renders it extremely valuable as charge material and being a product of sublimation is extremely reactive when subjected to the conditions found in the oxidizing furnaces.

The method of charging the furnaces varies with atmospheric conditions and the life and temperature of the furnace, charges being formulated to meet these conditions.

By following the charge from the raw materials to the finished products, the general working conditions can be best understood.

The oxidizing furnaces, two being considered a unit, consist of oval iron water-jackets, four feet in height, open at both ends, the upper end being five feet in length and three and one-half feet in width.

This water-jacket is securely built in a brick structure, on a solid brick base, and has a small opening in front which serves as a tap hole for the continuous removal of slag and metallic lead and their separation by the difference in their specific gravities. An oxidizing atmosphere is maintained by blowing air through tuyere holes entering near the base of the furnace. The feed door of suitable size and form is placed at one side of the furnaces.

The brick work surrounding the water-jacket or furnace proper is extended upward so as to form a large combustion chamber, which is in some cases water-jacketed.



View of the furnace with combustion chamber above. The trough for the separation of metallic lead from slag is seen in front of the furnace.



View showing "beehive" with "goose-necks" in the distance.

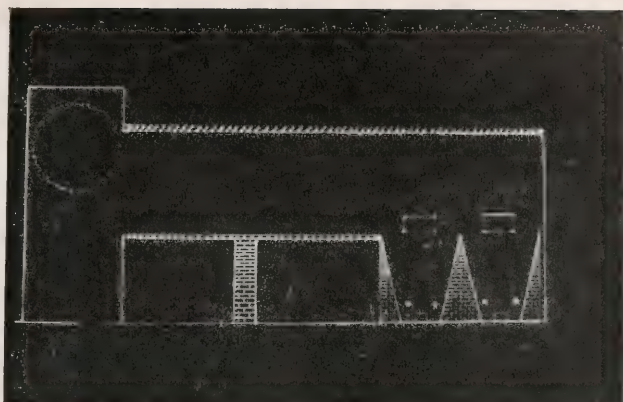


Diagram showing the location of the furnaces in relation to the combustion chamber and "beehive."

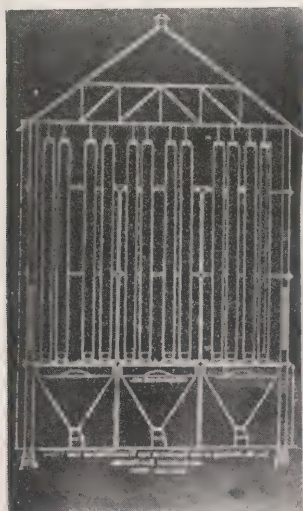


Diagram showing the arrangement of the bag room.



The hoppers into which the sublimed white lead falls from the bag room.



Immediately upon feeding the charge into the furnace, the fire of which is maintained at a point of incandescence, the reactions theretofore described occur with great violence and the volatilized lead passes upward into the combustion chamber.

Suction is maintained by a powerful fan placed between the bag room and the "goose-necks" which draws the condensed fume onward through the cooling system, finally driving it into the bag room where it is deposited.

The cooling system is built so as to produce maximum cooling effect by the introduction of baffles which prevent the easy passage of the fumes into the bag room. After the fume has passed out of the bee hive, where it is condensed and purified, it is drawn through the "goose-necks," large inverted U shaped pipes resting on hoppers, by the large suction fans and thence forced into the bag room.

The bag room is of a special type somewhat similar to those used in the collection of all fumes.

In the sublimed white lead bag room, however, are found three rows of hoppers (Cut #5), each hopper carrying 24 bags. The pressure of the fan forces all the gases through the cloth of the bags, while the sublimate is deposited. Occasional shaking throws the fume into the hopper where it is packed for shipment.

Sublimed white lead as it is removed from the hoppers is white in color. Much fume, however, which is unsatisfactory and not suited for use in the various arts is deposited in the portion of the cooling system preceding the suction fan. This fume is contaminated with a small percentage of coke, ash and other impurities, and being of a higher specific gravity than pure sublimed white lead, is readily deposited before reaching the fan, by a careful adjustment of the suction. The fume becomes darker in color the nearer the approach to the furnace. As a charge material the sublimate is excellent owing to its very finely divided condition.

Sublimed white lead, being a fume product consists of very fine amorphous particles, in size about one thirty-five thousandth of an inch in diameter. Its specific gravity is found to be 6.2.

In composition it shows approximately 78 per cent. of lead sulphate, 16 per cent. of lead oxide and 5.5 per cent. of zinc

oxide. That the lead oxide present is chemically combined as a basic sulphate of lead, the sulphate of lead present in excess of the amount required for the theoretical formula being present as neutral sulphate of lead, is held by practically all authorities. Chevalier claims the formula of  $Pb_3S_2O_9$  for the fume resulting from a furnace roasting lead sulphide.

According to Toch,<sup>1</sup> we find, that "A Mixture of precipitated lead sulphate, litharge and zinc white is approximately the proportions found in sublimed lead, when ground in oil and reduced to the proper consistency, dries totally different from sublimed white lead; in fact, sublimed white lead when ground in raw linseed oil takes two days to dry dust free, but the mixture just cited will dry sufficiently hard for repainting in twelve hours, because lead sulphate is a fair dryer and lead oxide a powerful one. The oxysulphate having the same composition, behaves totally different from the mixture." A mixture of the neutral lead sulphate with two per cent. of sublimed litharge, the finest and palest oxide of lead yet prepared, shows a yellow color not approached by any sublimed white lead yet made.

When sublimed white lead is subjected to the heat of the blow pipe it is only reduced to metallic lead, when intimately mixed with charcoal, with the greatest difficulty. It shows only slight darkening in an atmosphere containing appreciable amounts of hydrogen sulphide gas. When used in colored paints containing chemically reactive tinting materials it exhibits chemical inertness. The tinctorial power and opacity is directly lowered with a decrease in the percentage of lead oxide.

When chalking is noted in paints containing high percentages of sublimed white lead, it is found to differ from that noted in the case of other white lead pigments. According to Holley,<sup>2</sup> we find, "When ordinary white lead begins to chalk vigorously, it will be found that the paint film has lost its elasticity, and has become brittle and friable throughout; also, that the luster of the film under the chalk-like coating has entirely disappeared. A sublimed white lead film, on the other hand, retains much of its original elasticity under the chalk coating, indicating that the

<sup>1</sup> Chemistry and Technology of Mixed Paints: Maximilian Toch, page 19.

<sup>2</sup> Zinc and Lead Pigments: Holley, page 115.

disintegration is confined to the surface, and it is possible that the retention of the 'chalk' on the surface gives some protection to the unaffected coat below."

The pigment in common with other white lead compounds, finds its greatest value when compounded with zinc oxide and a small percentage of inert pigment of a crystalline nature, as these pigments tend to overcome those factors which militate against the use of the pigment alone.

Sublimed white lead is a pigment extensively used in the compounding of the finer grades of rubber goods.

The pigment has been found to practically inhibit corrosion on iron and steel even after long exposures, and ranks favorably with all other pigments yet prepared for the elimination of this decay. In consequence, it is rapidly finding its predicted place among paint pigments not only as a protective coating for wood but as a preservative for iron and steel.



(Abstract)

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THE EXAMINATION OF THE OLEORESINS FROM  
SEVERAL SPECIES OF PINE NATIVE TO  
THE WESTERN STATES

BY A. W. SCHORGER

*Forest Products Lab., Madison, Wisconsin*

*Western yellow pine (Pinus ponderosa) from California*

The oleoresin had a specific gravity of 1.0290 at 15° and gave on analysis: volatile oil 18.5%; rosin 79.5%; trash 0.8%; water 1.2%. The volatile oil had the following properties:  $d_{15}^{\circ}$ .8625;  $n_{D15}^{\circ}$  1.4772; and  $[a]_D = -41.34^{\circ}$ . About 70% distilled between 168–172° and consisted largely of Beta-pinene as proven by oxidation to nopinic acid m. p. 126°. Alpha-pinene was isolated from the first fraction: m. p. of nitrosochloride 103°; m. p. of nitrolpiperidine 118°. Limonene was isolated from the fraction boiling between 174–178.6° by means of its tetra-bromide m. p. 104°, and dihydrochloride, m. p. 50° C.

The rosin contains about 90 per cent abietic acid crystallized from alcohol and hydrochloric acid; m. p. 159–160°;  $[a]_D = -225.39^{\circ}$ ; formula  $C_{20}H_{30}O_2$  determined from analysis of its silver salt. Resin crystals obtained from the colophony by crystallization from acetone only melted at 155°. The rosin distilled between 245 and 265° C. at 22 mm. The crystals obtained from solution in acetone melted at 150–151°;  $[a]_D = -156.82^{\circ}$ . The original rosin had the following properties:  $d_{15}^{\circ}$  1.068; acid No. 148.8; sap. No. 161.3; ether No. 12.5.

*Western yellow pine (P. ponderosa scopulorum) from Arizona*

The oleoresin contained: volatile oil 19.6%; rosin 75.0%; trash 3.8%; water 1.6%. The volatile oil had the following properties:  $d_{15}^{\circ}$ .8639–.8672;  $n_{D15}^{\circ}$  1.4723–1.4729;  $[a]_D = +36.96^{\circ}$  to  $+37.44^{\circ}$ . It contained from 60–70% Alpha-pinene, m. p.



of nitrosochloride  $103^{\circ}$ ; about 5% of Beta-pinene, m. p. of nopinic acid  $125^{\circ}$ ; and 20-25% limonene, m. p. of tetrabromide  $104.5^{\circ}$ ; of dihydrochloride  $50^{\circ}$ .

The rosin,  $[\alpha]_D = -88.93^{\circ}$ , contained about 90% abietic acid crystallized from alcohol and hydrochloric acid; m. p. of abietic acid crystals  $159^{\circ}$ ;  $a_D = -252.35^{\circ}$ ; formula  $C_{20}H_{30}O_2$ , determined from analysis of silver salt.

*Digger pine (P. sabiniana)*

The oleoresin had:  $d_{15^{\circ}} 1.0265$ ;  $a_{D20^{\circ}} = -3.62^{\circ}$  for an 8.45% alcoholic solution. It gave on analysis: volatile oil 11.4%; rosin 83.5%; trash 3.3%; water 1.8%. The volatile oil had the following properties:  $d_{15^{\circ}} .6971$ ;  $n_D 1.3903$ ; b. p.  $96.1-98.8^{\circ}$  for the first 95%. The oil consists almost entirely of normal heptane since 90% had the following average values: b. p.  $98.5^{\circ}$ ;  $d_{15^{\circ}} 0.6881$ ;  $n_{D15^{\circ}} 1.3898^{\circ}$ .

The rosin had the following properties:  $d_{15^{\circ}} 1.073$ ; acid No. 156.7; sap. No. 176.5; ether No. 19.8. The original rosin could not be crystallized. However, the product obtained by distilling the rosin under reduced pressure crystallized readily from acetone; m. p. of crystals  $151-152^{\circ}$ ; formula  $C_{20}H_{30}O_2$  from analysis of silver salt. Resin crystals obtained from the crude oleoresin using acetone as the solvent melted at  $131^{\circ}$ ;  $[\alpha]_D = -274.91^{\circ}$ ; when crystallized from alcohol and hydrochloric acid the crystals melted at  $158-159^{\circ}$ . The silver salt contained 26.44% of Ag; calculated from  $Ag(C_{20}H_{29}O_2)$ , 26.37%.

*Sugar pine (P. lambertiana)*

The oleoresin,  $d_{15^{\circ}} 1.0420$ , contained: volatile oil 16.4%; rosin 75.3%; trash 3.4%; water 4.9%. The volatile oil had the following properties:  $d_{15^{\circ}} .8658-.8663$ ;  $n_{D15^{\circ}} 1.4727-1.4728$ ;  $[\alpha]_D = +29.93^{\circ}$ . The oil boiled largely below  $165^{\circ}$  and contained approximately 70-75% Alpha-pinene, m. p. of nitrosochloride  $103^{\circ}$ ; 5% Beta-pinene, m. p. of nopinic acid  $125^{\circ}$ ; 2-3% of a terpene, b. p.  $169-174.5^{\circ}$ ,  $d_{15^{\circ}} .8550$ , which appears to be phellandrene; 2-3% of what is apparently an aliphatic hydrocarbon, b. p.  $194-201^{\circ} C.$ ,  $d_{15^{\circ}} .7549$ ,  $n_{D15^{\circ}} 1.4249$ ; 10-12% of a sesquiterpene, agreeing closely with "aromadendrene" in color reactions

and physical properties: b. p. 250–255° at 739.9 mm.,  $d_{15^\circ}$  .9238,  $n_{D15^\circ}$  1.5006,  $[a]_D = +108.85^\circ$ .

The rosin had the following properties:  $d_{15^\circ}$  1.078; acid No. 142.7; sap. No. 152.6; ether No. 9.9. Crystalline resin acids were not obtained.

*Lodgepole pine (P. contorta)*

The oleoresin,  $d_{15^\circ}$  1.0210, contained: volatile oil 14.7%; rosin 77.7%; trash 2.5%; water 5.1%. The volatile oil had the following properties:  $d_{15^\circ}$  .8518–.8549;  $n_{D15^\circ}$  1.4860–1.4862;  $[a]_D = -57.81^\circ$ . The oil consists almost entirely of Beta-phellandrene. The rectified oil had: b. p. 60° at 11 mm.;  $d_{15^\circ}^{21}$  .8460;  $n_{D15^\circ}$  1.4861;  $[a]_D = -35.53^\circ$ ; m. p. of nitrite 103°.

The rosin had the following properties:  $d_{15^\circ}$  1.061; acid No. 131.2; sap. No. 139.6; ether No. 8.4. On crystallization from alcohol and hydrochloric acid about 80% of abietic acid crystals were obtained: m. p. 159–160°; formula  $C_{20}H_{30}O_2$ , from analysis of silver salt.

*Pinon pine (P. edulis)*

The oleoresin,  $d_{15^\circ}$  1.0238, contained: volatile oil 20.0%; rosin 76.5%; trash 0.9%; water 2.6%. The oil had the following properties:  $d_{15^\circ}$  .8680;  $n_{D15^\circ}$  1.4707;  $[a]_D = +55.35^\circ$ . It contains approximately 70–75% Alpha-pinene, m. p. of nitrosochloride 103°; about 5% Beta-pinene, m. p. of nopinic acid 123°; and 15–20% of d-cadinene having: b. p. 135–140° at 20 mm.;  $d_{15^\circ}$  .9173;  $n_D$  1.4925;  $[a]_D = +44.28^\circ$ . The cadinene dihydrochloride melted at 118° and gave  $a_{D20^\circ} = -5.43^\circ$  for a 5.94% ethereal solution.

The rosin had the following properties:  $d_{15^\circ}$  1.060; acid No. 155.2; sap. No. 164.1; ether No. 8.9. It distilled between 240–255° at 10mm. pressure. Neither the original rosin or distillate could be crystallized. With acetone as the solvent, crystals were obtained from the crude oleoresin, m. p. 129–130°; the latter when crystallized from alcohol and hydrochloric acid melted at 137°;  $[a]_D = -151.83^\circ$ ; the silver salt contained 26.46% Ag; calculated for  $Ag(C_{20}H_{29}O_2)$ , 26.37%. The rosin is assumed to consist of amorphous acids of the above formula.



# THE TECHNOLOGY OF VARNISH MANUFACTURE WITH NOTES ON AN IMPROVED SCIENTIFIC PROCESS

BY J. CRUICKSHANK SMITH AND GASTON DE PIERRES

*London, England*

It was in England towards the end of the 18th Century that the first varnish manufactory on a large commercial scale was established. In the early days of the industry, amber was the sole fossil resin employed. The amber was fused; to the fused mass was added some linseed oil; the whole was 'cooked,' and the solution of resin in oil was diluted with spirits of turpentine. Since that time an ever increasing number of fossil resins have been introduced into commerce and all have found some use in varnish making.

Today amber is but little used in the manufacture of varnish, and thus it has come about that while the chief raw material of the industry has changed the method of procedure by which the fusion, solution, and dilution are carried out has persisted without any important modification down to the present time. In Germany, Belgium, and even in England to a slight extent, several so-called improvements have been introduced. These consist for the most part in 'running' a small quantity of rosin in the gum-pot prior to the introduction of the hard resin. This procedure has been found to assist and expedite the fusion of the resin; but whether it can be described as an 'improvement,' in the technical sense, is a matter in which opinions differ.

In spite of the fact that varnish-making is a chemical industry very few chemists have devoted themselves with any degree of thoroughness to investigating the principles which govern it. On the other hand considerable attention has been paid to the chemistry and technology of linseed oil. It is true that Mr. C. Coffignier has conducted interesting investigations on the resins. He has determined their solubility in various media and their

acidity numbers, but although his results may form the starting point for further scientific research they have not as yet enabled us to put them to an industrial use. However, one fact appears to be established by Mr. Coffignier's researches, namely that the higher the acidity number of a resin the less satisfactory from a practical point of view is a varnish prepared from it. Arguing from this we might say that the best varnish would be produced by a resin which was as nearly as possible neutral, a condition which never obtains in practice. Kauri, it should be noted, is an exception to the rule.

If we consider the fusion of resin as it is effected in the ordinary process of 'running' in the gum-pot, it may be regarded as essentially a process involving partial dry distillation of polymerised terpenes. It may be likened to dry distillation of wood or coal with the differences that in the case of the resin the distillation is arrested at a definite point and that the valuable product is contained, not in the distillate (as in the case of wood or oil), but in the residue which is left in the gum-pot. As in the distillation of wood or coal the vaporised portion contains carbon dioxide and ethylic compounds while the distillate contains acetic and pyroligneous acids, naphthalene, hydrobenzene and, in short, that whole range of compounds derived from the polyterpenes to which we apply the name 'copal oil' or 'varnish fumes.' It must not be imagined that the acids which are found in the copal oil exist as such in the original resin, any more than acetic or oxalic acid is contained as such in wood or cellulose. The lower acids named are decomposition products, in the one case of cellulose and in the other of the polymerised terpenes.

The composition of copal oil varies comparatively slightly from whatever resin it is derived. The chief difference we have observed in various samples lies in their viscosity, which has no relation to the acidity number and which is determined by causes which will be dealt with later. It will be seen, then, that the usual process whereby a resin is fused or 'run' is one which results in a very definite decomposition and splitting of the complex polyterpene bodies contained in the resin.

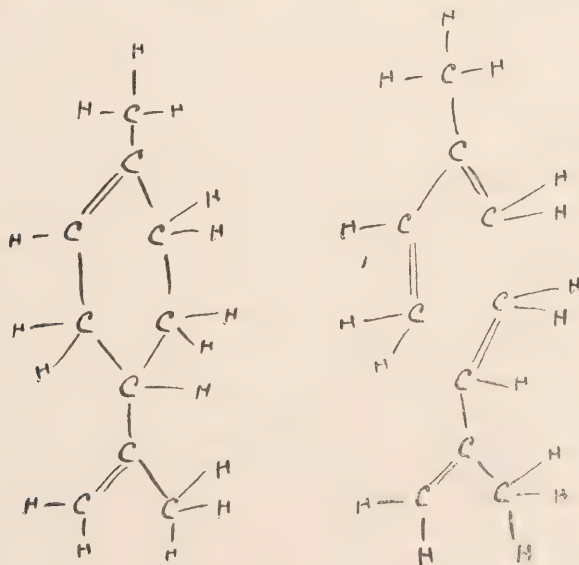
Nevertheless in the conventional method of varnish making this fusion and incipient distillation process could not be avoided



because the resin had to be rendered wholly soluble not only in spirits of turpentine but also in linseed oil, and this result could only be achieved (under the conditions which surround the conventional process) by subjecting the resin to strong direct heat.

The practical result aimed at in subjecting a hard resin to heat is to de-polymerise it, that is, to convert it into bodies of simpler constitution and lower molecular condensation than those possessed by the higher members of the polyterpene series. Thus the polymerised terpenes of high molecular weight which may be represented by the general formula  $(C_{10}H_{16})_x$  are in effect polymers of dipentene  $C_{10}H_{16}$  which again is a polymer of pentine (isoprene)  $C_5H_8$ , the first members of the series.

The splitting of a dipentene molecule into two pentine molecules by means of heat under suitable conditions may be expressed graphically thus:—



It must therefore be admitted that the conversion of a body of complex chemical constitution into bodies of simpler constitution by means of direct heat unmodified by any other condition cannot be regarded as technically correct inasmuch as it involves incip-

ient destructive distillation and an inevitable loss of sensible qualities of valuable raw material. The process of 'running' a resin, as carried out in the historic way, necessarily involves this result. The temperature produced in the gum-pot frequently approaches  $350^{\circ}\text{C.}$ , and no organic compound of complex constitution can withstand such a temperature without decomposition. In proof of this one need only recall that sometimes the contents of the pot take fire spontaneously. It is true that this happens but rarely when the operation is in the hands of an experienced gum-runner, but the fact that the phenomenon can and does occur affords conclusive proof that over-heating and consequently excessive decomposition do take place.

It would appear then that some modification of the conventional historic method of varnish manufacture might be adopted with advantage in order to eliminate the crude and wasteful decomposition of the resin. Consideration has convinced us that there are two fundamental points to be observed in order to obtain a result which will be scientifically correct and practically successful:—

(1) The addition to the resin in the pot of a substance of a stable nature possessing a low melting point whose function it is to envelop the particles of resin and protect them against over-heating.

(2) The discovery of a solvent which by dissolving the more soluble portion of the resin is capable of bringing about the solution of less soluble portions, just as alcohol brings about the solution of ether in water.

About sixty years ago Mr. Schutzenberger prepared a varnish by heating under pressure a mixture of copal, linseed oil and turpentine. But the product was unsatisfactory; it dried very slowly, remained tacky for a long time, and turned white when exposed to moisture. These results have been confirmed many times since and other processes involving simple solution under pressure have never, so far as we are aware, yielded satisfactory results. Mr. Henry Terrisse has investigated the cause of Mr. Schutzenberger's failure. He heated re-distilled spirits of turpentine under a pressure of 20 atmospheres for two hours in an autoclave at a temperature of  $295^{\circ}\text{C.}$  At the end of the operation

the autoclave and its contents were allowed to cool, when it was found that the pressure gauge still recorded a pressure of  $3\frac{1}{2}$  atmospheres. When the safety valve was opened the presence of a hydrocarbon gas was observed. The gas burned with a white flame and was found to possess properties characteristic of ethylene. The contents of the autoclave, which were originally spirits of turpentine, had been converted into a viscous oily liquid with a disagreeable empyreumatic odour. This liquid on distillation yielded fifty percent of volatile spirit, the remainder consisting of a gummy residue. Evidently therefore the original turpentine had undergone a process of resinification similar to but more complete than the resinification which takes place when turpentine is exposed to the air.

The experiment has been repeated, various hard resins being substituted for turpentine. Thus in the case of Zanzibar copal fused at  $300^{\circ}\text{C}$ . in an autoclave under a pressure of 14 atmospheres a pressure of  $1\frac{1}{2}$  atmospheres was registered when the temperature had fallen to the original figure. The liberated gas consisted almost wholly of carbon dioxide, and the fused gum residue was slightly tacky and somewhat friable in texture.

With congo similar results were obtained. A maximum compression of 20 atmospheres was registered, which fell to  $4\frac{1}{2}$  atmospheres when the autoclave was nearly cold. In this case the fixed gases produced were carbon dioxide and inflammable hydrocarbons. The fused residue from both the resins treated in this way were soluble in linseed oil, and varnishes made from them dried well and did not turn white in presence of moisture.

Finally linseed oil was heated in an autoclave at  $300^{\circ}\text{C}$ . The pressure registered scarcely rose above the normal. After two hours heating the oil became very tacky and dried with difficulty. This was probably due to some re-action in which acrolein and free glycerine play a part. These experiments appear to show conclusively that the flaw in Mr. Schutzenberger's process was the presence of turpentine. We arrive therefore at the following conclusions:—

(1) The ordinary hard resins are capable of being depolymerised with comparative ease under pressure.

(2) The process of fusion is however still too severe and causes decompositions which are undesirable.

(3) In order to ameliorate the process of fusion and prevent secondary decompositions there should be present some substance with a low fusion point which will dissolve the products of the fusion at the moment of and *pari passu* with their formation. In this connection it must be remembered that the complete fusion of a hard resin does not take place at one definite temperature (as in the case of a homogenous substance of definite chemical composition) but proceeds gradually throughout a range of 50 or even 100 degrees.

(4) Such a substance must be of stable constitution and not liable to decomposition under the conditions of fusing.

(5) It must be cheap and easily procurable.

At first phenol appeared to conform to these requirements and experiments made with it were quite successful. The price of pure phenol is however a drawback, and naphthalene was finally adopted as a material which conforms to the above mentioned requirements, and it has proved in every way satisfactory.

The pressure during the fusion need not exceed 6 atmospheres. When the process is complete and the autoclave is cold the pressure falls to normal. After the naphthalene has been removed by distillation the fused gum is found to be very hard, to be quite free from tack, and to be capable of being mixed with quite large proportions of linseed oil. The resulting varnish shows no tendency to crack and withstands the action of extremes of temperatures.

It is easy to conceive the 'mechanism' of the process described. When heat is applied the particles of resin become surrounded by an envelope of liquid naphthalene (the melting point of naphthalene being 79–80° C.). As each particle of resin fuses it is immediately dissolved by the liquid naphthalene and the process goes on until in a relatively short space of time the whole mass of resin, including the most insoluble constituents, is dissolved without any appreciable amount of local overheating or charring.

Here then we have a method of fusion and solution which



results in a depolymerised product without the production of copal oil which in the conventional method of gum-running is the inevitable product of the crude and destructive method which necessitates the loss of no small quantity of valuable material.

An interesting parallel case is that of the formation of salol. When salicylic acid is rapidly heated by strong direct heat it is converted into phenol with liberation of the total theoretical quantity of carbon dioxide. But if the heating is conducted gently on an oil bath there results a conversion of the salicylic acid into the chemically equivalent quantity of salol and no phenol is produced.

The method of which we have outlined the theory and which was originally suggested by Mr. Terrisse has been carefully examined by us. We have been able to confirm the practical results obtained by it and so far as our investigations have gone at present we find that all the ordinary hard resins of commerce can be satisfactorily and economically treated in the manner suggested.

We have also confirmed the work of Coffignier and Terrisse in other directions and have investigated the composition of copal oil. When distilled at normal pressure it yields between the temperatures of  $90^{\circ}$  and  $175^{\circ}$  C. distillates of an acid character in which acetic acid predominates. A small quantity of acetone is also given off. Between  $175^{\circ}$  and  $250^{\circ}$  the distillate consists of a brownish yellow oil of acid reaction and possessing an acrid penetrating odour. From  $250$  there is a sharp rise of the thermometer to about  $310^{\circ}$ , at which temperature there comes over a dark olive green oil. A continuous production of water occurs at this point. The thermometer then rises to about  $350$  and thenceforward the formation of water becomes copious, and the distillation is complete at about  $395^{\circ}$ . Nearly the whole of the copal oil can be distilled and the residue in the retort consists of a black tarry substance similar in appearance to bitumen and having an acid odour. The greenish oily distillate which comes over after  $250$  is muddy and has a disagreeable empyreumatic smell and gives an acid reaction. It has a density bordering on but always under  $1.0$ . On standing it quickly clarifies



and separates into two layers, the lower consisting of an aqueous solution of acetic acid and the upper consisting of a mixture of naphthalene or hydro-naphthalene and polyterpenes.

Entirely different results are obtained when the distillation is conducted under reduced pressure. At a pressure equivalent to 15 mm. of mercury under the normal a certain quantity of the lower acids come over between 50° and 75° C. The thermometer then rises rapidly to 150° when the distillate consists of a clear yellow oil of disagreeable odour but *not acid*. Another rapid rise takes the thermometer reading to 225° when a very clear greenish oil passes over. The odour of this fraction is pleasant and reminds one of that of old varnish. At 270° the distillation should be stopped because at this point the formation of water commences, which shows that the residue in the retort is beginning to decompose.

From a litre of copal oil the following quantities of the above-mentioned fractions have been obtained:—

|                         |                |
|-------------------------|----------------|
| Acid fraction . . . . . | 75 cc.         |
| Yellow oil . . . . .    | 200 cc.        |
| Green oil . . . . .     | 200 to 250 cc. |
| Residue . . . . .       | 475 to 525 cc. |

The residue consists of a fused gummy mass rather friable in nature, slightly tacky, and very dark in colour which reminds one (except as regards colour) of the fused product obtained by simple fusion of the resin in an autoclave. From this gummy residue quite good varnish can be made.

It is worthy of remark that all the samples of ordinary copal oil which we have examined yield similar results. From whatever species of copal they have been derived they always yield the same acid fraction, the same yellow and green oils and a solid residue. The solid residue alone varies.

Thus kauri and manilla yield very little residue; Congo yield much more, and so on.

The quantity of residue bears a definite relation to the melting point of the resin or rather to that of the most infusible component part of the resin, and has therefore a direct bearing on the viscosity of the copal oil. If the fusion and distillation





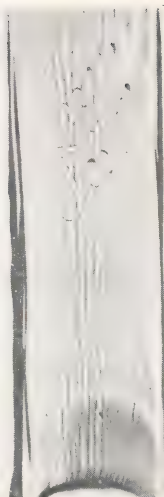




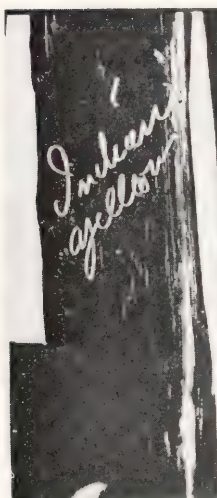
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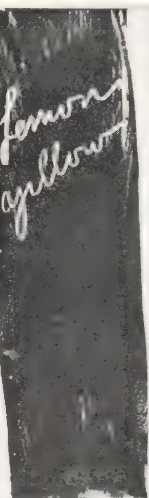
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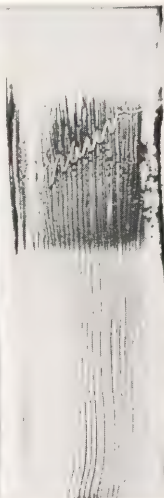
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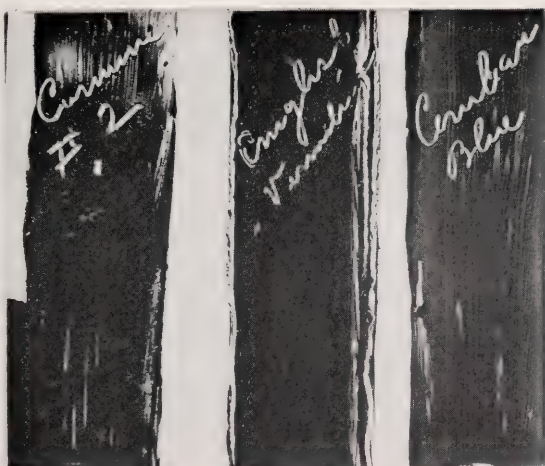
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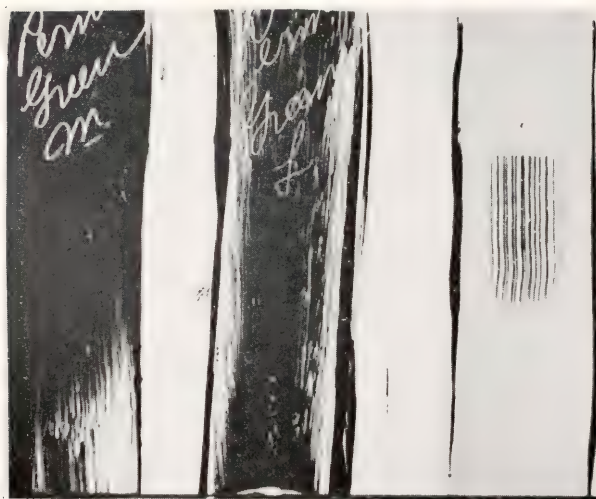
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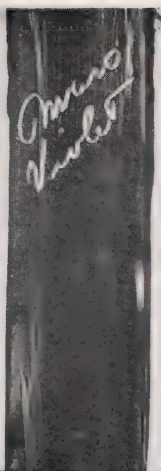
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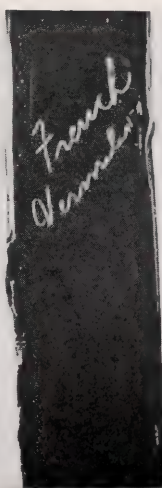
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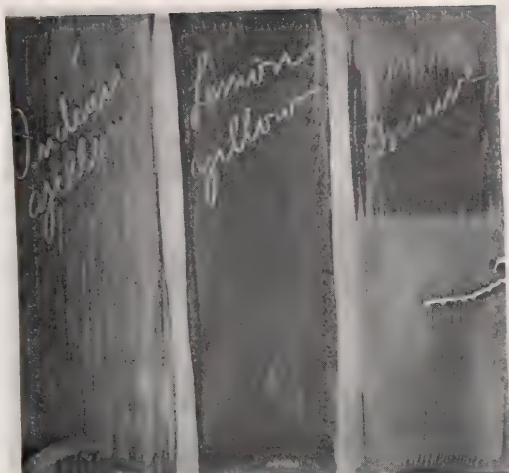
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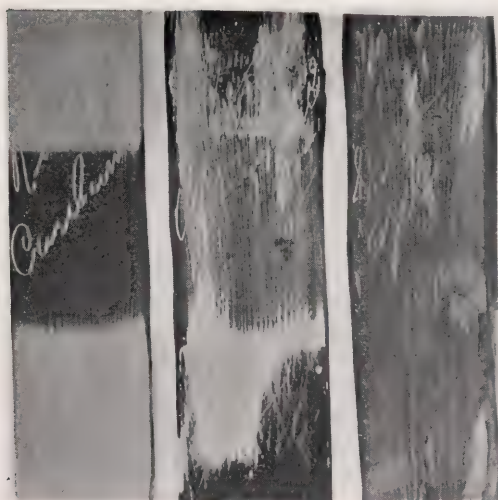
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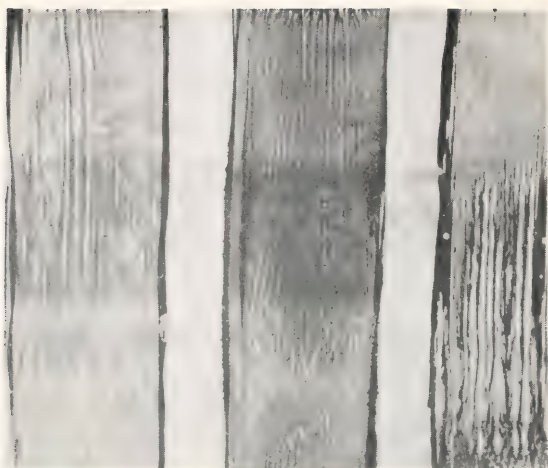
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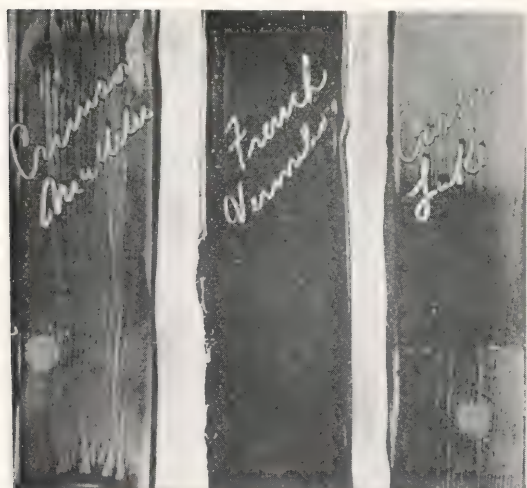
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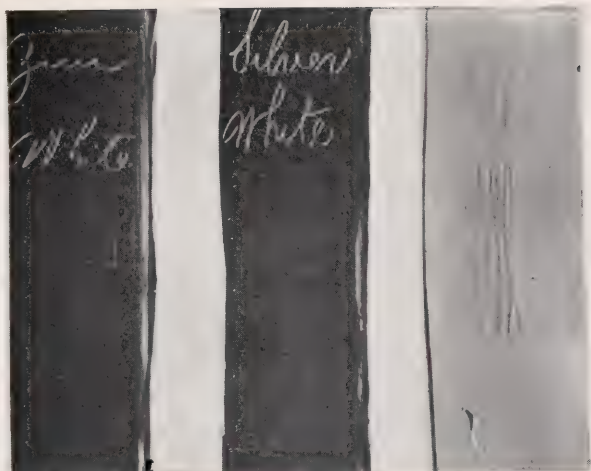
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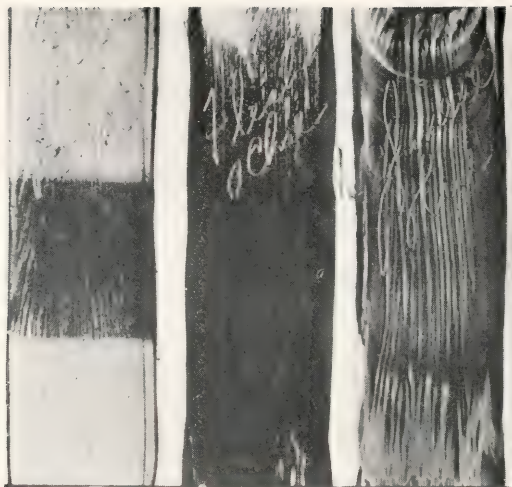
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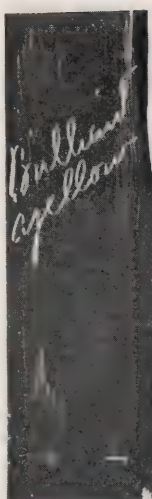


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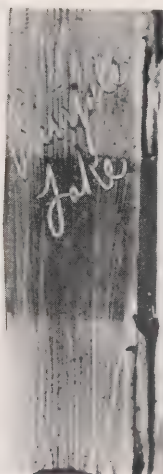
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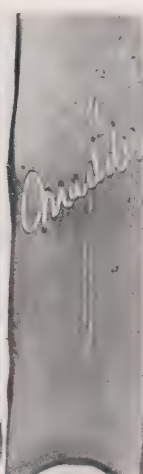
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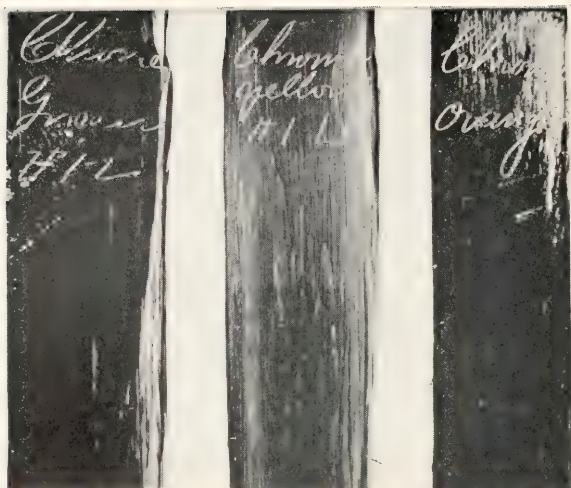
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are carried out with a resin to which has been added a proportion of colophony the acid fraction always increases.

From a survey of the foregoing facts we arrive at some practical conclusions :—

(1) Acids are produced by the action of heat on the hard resins and are found again when the copal oil is fractionated.

(2) The distilling off of the more fusible portion of the resin causes a part of the less fusible and therefore harder portion to be carried over. Just as naphthalene can be driven out of coal tar by means of steam so is part of the hard resin of high melting point carried over by the vaporised terpenes which are produced by the partial decomposition of the resin in question.

The solvent action of the two oily fractions last mentioned has been investigated. The green oil possesses powerfully solvent properties and it has also been established that the green oil is carried over without decomposition by vaporised naphthalene.

In practical varnish-making by the autoclave process it is possible therefore to employ a mixture (in suitable proportions) of the green oil and naphthalene. The former acts as a powerful aid in bringing the hard resins into a soluble form, and the latter can be easily distilled off, carrying with it the added green oil. Hence in the case of certain resins the fusion in the autoclave can be avoided altogether and in other cases much lower temperatures can be used in the autoclave than would otherwise be the case with the result that the varnishes obtained are extremely pale.

It is not claimed that the work of an industrial nature which we have described has added much to our chemical knowledge concerning the nature of the hard resins but it has a very direct bearing on the theory and practice of varnish-making and is not without interest in a large group of chemical industries. Our experiments at any rate go to show that the resins commonly used in varnish-making are similar in their general composition and probably also in their constitution and that they consist essentially of assemblages of polymerised terpenes. We claim that there is abundant evidence at hand to warrant the dissipation

of the fiction that the historic conventional method of gum-running is a necessary or even a defensible process inasmuch as the "acid" which the old fashioned method strove to separate was to a large extent produced by the incipient destructive distillation of the resin itself. We claim also that the depolymerisation (on which the solubility of the fused resin depends) can be brought about by a method which is more gentle in its effects, more under scientific control and capable of producing better and cheaper varnishes than the method which has been the fetish of the mystifier and secret-monger for upwards of two hundred years.

In conclusion we should like to point out that in spite of the apparent simplicity of the process and of the principles on which it depends it must be controlled with skill and nicety in order that satisfactory and uniform results may be obtained. The merely theoretical worker who attempts to make good varnish either by this or by any other process will find that he has a long and costly novitiate before him. When it will be granted that the modern varnish factory has little use for the hide-bound rule-of-thumb, so-called practical man, it is equally true that to the dough of organized science must be added the leaven of practical skill—that indefinable turn of the wrist which will always distinguish the clever cook, the good varnish maker, and the successful technical expert.

## THE PERMANENCY OF PAINTING

BY MAXIMILIAN TOCH

*New York*

We are all familiar with the phenomenon that mineral substances which have a distinctive coloring with the exception of one or two which will be mentioned later, show no change of color, and as far as we know have not changed in their appearance for ages. Many of these mineral substances have been used for centuries for decorative purposes either as pigments or as tints. Some of the artificial pigments such as Madder Lake, Bone Black, Lamp Black, Ultramarine Blue, Siennas and Umbers which are simply used to produce their particular shade, have all been regarded as more or less permanent, and are permanent particularly when used alone, and yet, when these pigments are mixed with a drying oil medium they decompose to some slight extent, sometimes through the aid of the decomposition products of the medium, and sometimes because of the influence of brilliant light, darkness, or the gases generated in a large city.

All of the experiments which we have made are not so much for the purpose of proving what is already well known, that certain pigments when exposed to the light change, or when mixed with others to produce chemical effects which are different from their original, but for the purpose of suggesting a remedy which up to now has been more or less empirical, and as far as we know has never been worked out satisfactorily.

Everyone deplors the decomposition of the master pieces of modern paintings, and at the outset it must be impressed upon those who are interested in the subject, that an oil painting of moderate size can be thoroughly protected against the influence of light and noxious chemical gases in the atmosphere, if the back of the painting is thoroughly coated with a non-absorbent or waterproof medium, and if the face of the painting be coated with a hard flexible varnish and the whole hermetically sealed in



a frame with a glass cover, but we are not dealing with prophylactics. We are dealing with remedies, and to that end we exposed a large number of oil pigments on the market under glass, and each pigment was coated on the glass in strips of 3'' long and 1 inch wide, and the centre inch covered with black paper close to the pigment so that light would have no access.

The following is the tabulated result of the photographs obtained:

Illustrations 1, 2 and 3 are well known examples of the work of Sir Joshua Reynolds in the Metropolitan Museum of Art in New York City.

Sir Joshua Reynolds seldom painted two pictures alike. He was continually experimenting with pigments which would secure for him as he thought greater permanency, and as he possessed insufficient knowledge of the composition of the materials with which he worked, he very often mixed pigments which interacted such as ochre and madder lake.

Illustration No. 1 is almost mono chromatic, it having faded into a monotone.

Illustration No. 2 is in a fairly well preserved condition, and the red lips of the child are still red.

Illustration No. 3 has bleached out completely, until the face, breast and fur trimming of the dress are all reduced to the same tone and practically the same color value, and the upper line of the red lips show no line of demarcation. The face and flesh color is practically anaemic in this picture. What was once the portrait of a handsome healthy looking woman is today one mass of faded color.

No. 4 Venetian Red shows no fading.

No. 5 Indian Red shows no fading.

No. 6 Terre Verte is permanent.

No. 7 Indian Yellow is permanent.

No. 8 Lemon Yellow is permanent.

No. 9 Mauve Lake disappeared entirely in four months, excepting in the centre where it was protected from the light.

No. 10 and 11 are two kinds of Brazil wood red which were made up to simulate the lakes used by Sir Joshua Reynolds. They both bleached badly in a short time.

No. 12 is the new color called Harrison Red which is about ten times as strong as English Vermilion. This is a very permanent pigment.

No. 13 is Payne's Grey, a very fugitive color.

No. 14 Yellow ochre which has grown slightly darker on exposure.

No. 15 Yellow lake which is very badly faded.

No. 16 Sepia, not very permanent.

No. 17 Rubens madder. This is evidently a proprietary name, and cannot be a true madder lake as it has faded completely in four months.

No. 18 Magenta Lake very badly faded.

No. 19 Rose Carthame. Not a vestige of this color remained.

No. 20 Ultramarine Blue. This pigment becomes more brilliant on exposure, and darkens considerably when hidden from the light.

No. 21 Strontium Yellow, very permanent.

No. 22 Madder carmine, fairly permanent.

No. 23 Malachite Green, permanent.

No. 24 Mars Yellow, permanent.

No. 25 Carmine 2, fugitive.

No. 26 English Vermilion, darkens considerably when exposed to light, but remained permanent when not exposed.

No. 27 Cerulean Blue, becomes more brilliant when exposed to light.

No. 28 Alizarine Yellow, evidently a misnomer, but is a yellow lake which fades very rapidly.

No. 29 Carnation Lake, entirely bleached in four months.

No. 30 Alizarine Green, evidently a misnomer. It is an aniline green lake, not permanent.

No. 31 and 32 Permanent Green, Medium, and Permanent Green, Light, very permanent colors.

No. 33 Bitumen, evidently not genuine bitumen, as it has completely faded and lost its glaze, for genuine bitumen usually turns dark and shows cracks.

No. 34 Perfect yellow, permanent.

No. 35 Mars Violet, permanent.

No. 36 Black Lead, permanent.

- No. 37 Crimson madder, permanent.  
No. 38 French Vermilion, darkens on exposure.  
No. 39 Carmine lake, faded badly.  
No. 40 Madder lake, deep, shows very slight sign of fading.  
No. 41 Madder lake, pale, shows slight signs of fading.  
No. 42 Lemon yellow, permanent.  
No. 43 Permanent yellow, permanent.  
No. 44 Yellow lake, bleached completely when exposed to the light.  
No. 45 Violet Carmine, permanent.  
No. 46 Indian yellow, permanent.  
No. 47 Lemon Yellow, permanent.  
No. 48 Mauve, very fugitive.  
No. 49 Rose Carthame, very fugitive.  
No. 50 Ultramarine, becomes more brilliant on exposure.  
No. 51 Strontium yellow, very permanent.  
No. 52 Burnt Umber, contains a lake and shows signs of fading.  
No. 53 Bone brown, not permanent.  
No. 54 Mummy, not permanent.  
No. 55 Crimson madder, permanent.  
No. 56 French Vermilion, permanent, but darkens slightly.  
No. 57 Carmine lake, fugitive.  
No. 58 Zinc white, permanent.  
No. 59 Silver white, permanent.  
No. 60 Rose Dore, fugitive.  
No. 61 Sepia, fugitive.  
No. 62 Rubens madder, fugitive.  
No. 63 Magenta lake, fugitive.  
No. 64 Yellow lake, Italian pink, fugitive.  
No. 65 Flesh Ochre, permanent.  
No. 66 Chinese blue, permanent.  
No. 67 Cobalt yellow, permanent.  
No. 68 Cobalt blue, permanent.  
No. 69 Green lake, fugitive.

This green lake which was originally a bright green, changed into a true blue showing that it was made of a permanent blue and yellow lake, the yellow lake having bleached completely.

- No. 70 Brilliant yellow, permanent.
- No. 71 Mummy, fugitive.
- No. 72 Transparent black, permanent.
- No. 73 Purple lake, fugitive.
- No. 74 New Blue, becomes much more brilliant on exposure.
- No. 75 Purple madder, permanent.
- No. 76 Chrome green, permanent.
- No. 77 Chrome yellow, darkens on exposure.
- No. 78 Chrome orange, permanent.
- No. 79 Cadmium, pale, permanent.
- No. 80 Cadmium, deep, permanent.
- No. 81 Emerald green, slightly fugitive.

Many of these colors were duplicated in exposure, and where, for instance, I have given #19 as rose carthame, and #49 as rose carthame, it was due to the fact, that they are the same color but made by two different manufacturers.

All of these exposures were made by pasting a black strip of paper across the middle of a three inch stripe of color, and serve to indicate the effect of light such as would reach a painting inside of a building.

We have not dwelt on the effect on the ultra-violet rays on pigments of this kind, because glass is apparently a permanent bar to these rays.

Yellow lake composed of the quercitron extract precipitated on an alumina base had bleached out completely so that at the end of four months there was nothing left in the bleach to show any trace of color.

The vermilion known as English vermilion which has always been regarded as a perfectly permanent pigment had turned perfectly brown where exposed to the light and remained brilliant where sheltered from the light. This particular experiment was carried out away from any noxious gases, so that the effect produced in this case is one of light entirely.

Yellow ochre alone showed no decomposition whatever.

Green lake which in this instance was a transparent blue similar to artificial cobalt colored with a green dye, became reduced to a perfect blue at the end of four months where exposed to the light but showed no change when protected from the light.

One of the bitumens,—and bitumens notoriously blacken in the light—had bleached out completely, showing that it was an artificial material and not the natural bitumen.

Carmine lake had suffered materially having bleached almost completely when exposed, and French vermilion had blackened much more than the English vermilion.

Crimson madder which in its dry state and as a water color showed no decomposition, began to show a slight deterioration at the end of four months.

The so-called mauve lake disappeared entirely. The mixtures of madder and carmine known as Madder Carmine were also seriously affected.

Prussian blue was one of the most permanent.

Gamboge was much more permanent than was to be expected, but Purple lake was very much bleached and Purple madder considerably affected.

All the artificial ultramarines under their various names seemed unchanged when viewed by transmitted light, whereas a change was quite visible when they were seen by reflected light.

The new pigment known as Harrison Red which has been described in another publication showed no decomposition and the artificial alizarines such as Alizarine Crimson and Alizarine Scarlet which are identical with the natural mediums, showed no trace of fading.

The oxides of iron, such as Indian Red, all of which have a chemical composition of  $\text{Fe}_2\text{O}_3$  Ferric oxide, are changed into a different form, probably  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ . This is particularly noticed when these pigments are mixed with oil media.

Italian pink which is similar to the lake colors, bleaches out entirely, and the brilliant scarlet red known as Rose Carthame suffered such decomposition that not a trace of it was left.

The colors affected by sulphur fumes in the atmosphere such as chrome yellow, chrome green, prussian blue, paris green, emerald green, flake white and white lead when protected from the air showed no decomposition whatever when exposed to light.

All of the blacks, such as lamp black, carbon black, graphite, bone black, and vine black which latter includes all of the charcoals, show no trace of any change.



The illustrations accompanying this treatise were all made on pan chromatic plates which show the relative color value, and in which a faded red or a faded yellow is distinctly shown up and in which the color spectrum from the D line to the ultra red is perfectly visible.

I shall now show you the actual effect of light upon the various pigments treated in this paper, and the ortho chromatic photographs of the faded paintings and color decomposition. Colors were here shown in the stereopticon.

Pastels and water colors are notoriously more permanent than oil paintings. Once a color has become dry, there is nothing but the light to act upon it, but in an oil painting, there is in addition to the light, the generation of water, carbonic acid and formaldehyde, all of which would have the combined effect of decomposing, even to a slight degree, some of the pigments.



## MODERN PAINTING METHODS IN THE NAVY

BY HENRY WILLIAMS

*Brooklyn, N. Y.*

The considerations that lead to the use of paint on steel ships are the same in general as those necessitating its use on steel structures on shore. The conditions on ships, however, necessitate more urgent measures for preserving their structures. Corrosion of the steel in ships proceeds more rapidly than on shore and might result, if neglected, in the total loss of the vessels. Sea water, which contains in solution many elements, probably is the strongest corrosive agent with which large quantities of structural steel comes into contact. It, and the moisture from it, serve to set up the electrolysis necessary for corrosion. The black oxide mill scale, which is on all structural steel, unless special precautions have been taken to ensure its being removed, is electronegative to the steel and the corrosive action of the sea water is stimulated by its presence.

To a person not familiar with the effect of sea water on steel work, its power of disintegrating is not always apparent. It is so much greater than the corresponding action of fresh water that, by comparison, the latter may be neglected, and steel ships which are laid up in fresh water basins require little attention to prevent corrosion of their outside bottom plating.

Another characteristic of sea water, which it shares with fresh water, and which unfortunately has not been taken into account, is its action on those paints most generally used on shore and which are made up with linseed oil as a vehicle. Not being a chemist I will not attempt to explain this action beyond saying that the linseed oil film becomes softened by the action of the sea water and the paint ceases to protect the steel under it. As stated, this important defect of linseed oil paints has not been recognized generally either in the Navy or the merchant marine, and such paints continue to be applied on steel in locations exposed

directly to the action of salt water. Although there are many damp-proof and water-proof paints made commercially, their advantages do not seem to have been pointed out with sufficient clearness and force to bring about their general adoption for ship use.

Experience, however, has taught ship owners the world over that they must take energetic steps to prevent deterioration in protecting from corrosion the steel of their ships by the free use of paints, varnishes or cements. Naval vessels have an additional consideration for the use of paint in their desire and the necessity for neatness and cleanliness beyond that achieved ordinarily on vessels of the merchant marine.

Thus paint for the Navy is an important subject and its importance may be pointed out in a striking way by considering the amount and cost of paints used in some cases. During the construction of the 22,000 ton battleship *Florida*, up to the time of first commission there were used a total of about two hundred tons of paint and varnishes. Of this amount about one hundred tons was red lead paint used to protect the steel from corrosion, principally as priming coats, though in some cases it was used alone on the steel work, no finishing coat of paint being necessary. The total cost of all paint and varnish used including the labor of preparing the surfaces and applying the paint was over \$150,000. It should be borne in mind that this amount represents the first painting costs, the value of paints and varnishes used annually by a battleship of this size for keeping the ship painted, exclusive of cost of applying it, is not far from \$15,000.

The above will serve to give weight to my statement that to the Navy, and to the merchants who make a business of supplying painting materials, the general questions of paint used by the Navy, the kinds of materials used, the methods and frequency of application are of vast importance and deserve much more attention than they have received. The chemists who make it their business to determine the qualities and characteristics of paint materials could render an important public service by investigating the subject along scientific lines and telling those of us who are concerned with the use of the paint what are the consider-

ations affecting its choice and what materials can be expected to give best service in the various locations on shipboard. This has not been done heretofore, and shipbuilders use continually paints that not only are not the most suitable but that often serve no useful purpose and even stimulate corrosion. Many such examples could be cited, the most striking being the general use of linseed oil paints alluded to above, red lead paint being used perhaps most often in locations for which it is essentially unfit.

The policies of the Navy Department in the use of painting materials are very conservative and changes are not made readily. The responsible officials must be convinced that changes are desirable and in the interest of efficiency. Such conviction can be carried only by demonstration of superior merit in actual tests, which are scrutinized by persons generally not ready to be convinced easily. These tests of paint are made usually by application on a ship and the determination of comparative results by the same persons is not always possible, due to the removal of the ship to another station. This renders the decision dependent upon the observation of persons who may not be competent to decide and who are frequently not interested in the conclusions. Such tests naturally require several years to produce results and shifting personnel in the interval often nullifies the conclusions reached. The above should serve to indicate the difficulties attendant upon changes in the Navy Department's policies as regards the painting materials and methods prescribed for naval vessels.

In the purchase of its paint supplies, which exceed in value annually over one half a million dollars, the Navy Department makes use of specifications worded accurately to require in most cases the highest grades afforded by the market. Careful inspections and tests are made in most cases to ensure that the materials accepted are as specified. Many of the characteristics mentioned in the specifications no doubt are not essential to the purposes for which the materials are used and manufacturers often have seemingly just ground for complaint in the rejection, for technical deficiencies, of materials which they feel assured would answer fully all practical needs. On the other hand it must be remembered that there is very little authoritative data as regards paint



materials and on which specifications may be used. The naval authorities consequently have been forced to draft their own specifications and apparently they have erred only in doing their work too well and in not accepting changes in ideas until there was in their opinion ample assurance that such changes met with the approval of the trade generally. For this reason some of the Navy's paint specifications have not been changed in many years. The Navy has inherited the traditional conservatism of the practical painter and for many years adhered to the old and staple paint materials, such as red lead, white lead, white zinc, pure linseed oil and pure turpentine. This fact long has been used as an argument against the newer paint materials. Many manufacturers regard the Navy trade so highly as a recommendation of their products that they are willing often to sell them at a slight loss to ensure receiving the contracts, as the care exercised by the naval officials is accepted by the public as an index of merit of those materials that are purchased and accepted. The fact that the Navy Department requires the use of certain paint ingredients doubtless has influenced many ship owners and others to purchase and use the same materials.

In the past five years the naval authorities have awakened to the advances that have been made in the paint trade and have taken some progressive steps, with others in contemplation, and promise to place themselves in the ranks of the progressive paint users.

One of the most important advances in recent years was the change from the custom formerly in vogue of issuing to each naval vessel its paint in the form of the raw ingredients, which then were mixed on board ship by hand as required for use by the ship's painter. Now paint, mixed and ready for use after stirring, is issued. This change was one of the most important and far reaching in its effect that could have been taken. It recognizes primarily the superiority of the compound paints made by machinery according to certain definite formulas over that mixed at haphazard according to the whim of the comparatively ignorant painters on the ships. This, however, was not the most important consideration in making the change. It was recognized that the cost of the Navy's paint could be reduced, without

impairing its quality, by using some of the newer paint materials. This would not have been possible had the ingredients been issued to the painter, for they would have been condemned before even tried. As it stands paints have been made up, issued and used with good results on naval vessels, which contained such ingredients as blanc fixe, barytes, silica, lithopone, petroleum thinners, China wood oil, fish oil, soya bean oil and other materials that many persons regard as rank adulterants. The fetish which binds seafaring men to the use of red lead linseed oil paint has been discredited and paints which cost much less giving better results are being used extensively in its place.

The most important of the changes in materials, that has been made up to the present time, is the discontinuance of the use of turpentine as a thinner for paints. This change was made after full investigation and consideration of the question in all its phases. During the year 1910 the Navy purchased over 70,000 gallons of turpentine at an average cost per gallon of over 78 cents. Early in 1911 the change was instituted and now a hydrocarbon spirit made from petroleum is used almost exclusively for thinning paint. This important step no doubt has had an influence on the trade in general and it is to be hoped that it will serve to reduce the total consumption of turpentine and tend to a conservation of the pine forests being destroyed by the turpentine people to meet the fancy of painters who think it is essential to make good paints and varnishes. This change was not made without opposition, not only from the turpentine manufacturers, but from within the service itself. Many of the master painters in the navy yards attributed to the turpentine substitute faults in the paints that were shown readily to be due to other causes. The ships' people opposed it because they thought that, as the paints issued to them cost less as a result of the use of the substitute, they were consequently less efficient.

Another innovation that has been made is the introduction, for use preliminarily on one division of the battleship fleet, of a slate color outside paint, having its pigment made of zinc oxide and blanc fixe, with necessary tinting materials. This paint is

intended to supplant the lead and zinc paint slate color used for many years; on tests which have been extended over more than one year it has shown excellent qualities of resistance to the action of salt water, while costing about 35 cents per gallon less than the lead and zinc paint.

Another question affecting paint that has been engaging the attention of the naval authorities recently is lead poisoning as caused by the use of lead paints. There have been a number of cases not only among the navy yard workmen but among the crews of the ships. Many of the spaces on shipboard are so confined and men scaling off old paint or applying new paint come into such close contact with it that they are susceptible especially to lead poisoning. It is regarded as being probable—though the number of well defined cases of plumbism is comparatively small—that there are many persons who suffer from liver trouble, more or less acutely, as a result of absorption of lead by their systems, due to the exaggerated use of lead paints on shipboard.

In closing I cannot refrain from making mention of the situation as regards shipbottom paint in the Navy. As may be understood readily the Navy is a large consumer of this class of paint. For many years it purchased its supplies from various firms, who manufactured under trade names and secret formulas and who claimed wonderful properties for their products. They affected such a great mystery as to the ingredients and methods of manufacture, that for many years it was assumed to be necessary to buy shipbottom paint and pay the exorbitant prices asked. Consideration finally led to the conclusion that perhaps it would not be so difficult to make the paint and, after experimenting a number of years, a satisfactory formula was evolved, which has given most excellent results and has served to reduce the annual expense for shipbottom paint for naval vessels by many thousands of dollars. The change naturally has met with great opposition from the persons who were interested in the contracts under which the shipbottom paint supplies were purchased formerly. In spite of the opposition, the policy has been adhered to, and to-day the Navy manufactures at Norfolk annually over 60,000 gallons of shipbottom paints. This not only has effected a considerable

saving, estimated to exceed \$100,000 annually, but the practical results obtained in preventing the fouling of the bottoms of the ships are uniformly satisfactory, which is more than can be said of the results obtained from the paints that were purchased formerly.





## SUR DEUX NOUVELLES SOURCES DE PINENE

PAR M. VÈZES

*Professeur à l'Université de Bordeaux, Bordeaux, France*

Au moment où, par suite des besoins croissants de l'industrie, on commence de viviers cotés à exploiter de nouvelles variétés de pins en vue de la production de l'essence de térébenthine, il paraît utile de soumettre à une étude méthodique la matière première de cette fabrication, c'est à dire l'oléorésine ou gemme secrétée par chacun de ces arbres. Cette étude comparative des gemmes de diverses variétés de pins est utile à un double point de vue: d'une part, elle fournit aux industriels des indications sur le rendement en essence volatile des gemmes qu'ils sont appelés à distiller; d'autre part, elle permet de voir quelles sont, parmi les essences volatiles ainsi extraites, celles qui possèdent la composition et les propriétés de l'essence de térébenthine, et par suite ont réellement droit à cette dénomination. Les essences volatiles que fournit la distillation aqueuse de la gemme des pins sont en effet assez différentes les unes des autres par leur composition, et par suite par la manière dont l'industrie peut les utiliser, pour qu'il soit nécessaire de faire entre elles des distinctions: dans ce qui va suivre, nous réserverons, comme l'a fait le Deuxième Congrès international pour la répression des fraudes (Paris, octobre 1909), le nom d'essence de térébenthine à celles de ces essences dont les constituants principaux sont le pinène et le nopinène, c'est à dire dont la majeure partie (80% au moins) passe à la distillation, sous la pression atmosphérique normale, entre 154° et 164°. <sup>1</sup>

Dans un mémoire antérieur<sup>2</sup>, nous avons indiqué les premiers résultats de cette étude en ce qui concerne la gemme de Pin d'Alep; l'examen de nouveaux échantillons de gemme de même origine va nous permettre de compléter, en les confirmant, nos

<sup>1</sup> Compte rendu de travaux du Congrès de Paris, pp. 846 et 1297.

<sup>2</sup> Bull. de la Soc. chim. de France, (4° série), t. 5, p. 931; 1909.

conclusions premières. Nous donnerons ensuite les résultats de l'examen analogue que nous avons eu récemment l'occasion de faire de gemmes de *Pinus Massoniana*, et nous verrons que ces gemmes constituent, comme celles de Pin d'Alep, une matière première avantageuse pour la préparation du pinène pur.

1.—On sait que le Pin d'Alep (*Pinus halepensis* Mill.) est exploité en Grèce, en Algérie et dans le midi de la France. Le tableau ci-dessous donne la composition immédiate des échantillons de gemme, provenant de cet arbre, qui nous ont été envoyés d'Algérie et de Provence.

| Echant. n° | Essence | Produit sec | Impuretés solides,<br>eau et perte |
|------------|---------|-------------|------------------------------------|
| 1          | 27,0%   | 66,7%       | 6,3%                               |
| 2          | 17,3    | 71,9        | 10,8                               |
| 3          | 14,7    | 78,3        | 7,0                                |
| 4          | 23,0    | 70,0        | 7,0                                |
| 5          | 30,0    | 66,0        | 4,0                                |
| 6          | 25,9    | 63,1        | 11,0                               |
| 7          | 20,3    | non dosés   | .....                              |
| 8          | 17,6    | d°          | .....                              |

Dans ces échantillons, le rendement en essence varie, comme on le voit, du simple au double (de 14,7% à 30%). Ces variations paraissent tenir surtout au soin avec lequel la gemme est récoltée, et en particulier au temps plus ou moins long pendant lequel elle reste exposée à l'air. La comparaison des trois derniers échantillons (n° 6, 7, 8) est à cet égard particulièrement instructive: ils ont été récoltés, dans des conditions similaires et garantissant tout particulièrement leur authenticité,<sup>1</sup> sur les mêmes arbres de la forêt domaniale de Touazizine (Algérie), à des époques différentes d'une même saison de résinage (7 juin, 20 août, 11 novembre); la distance que les gouttes de gemme avaient à franchir sur l'arbre avant de parvenir dans le pot était faible en

<sup>1</sup> Nous sommes heureux de renouveler ici nos remerciements à M. Laporte, Conservateur des forêts à Oran, auquel nous sommes redevable de ces échantillons de gemme, ainsi que de l'un des échantillons d'essence dont il est question plus bas.

juin, plus grande en aout, plus grande encore en novembre; aussi voyons nous le rendement en essence baisser progressivement du premier au troisième de ces échantillons.

L'étude des essences provenant de la distillation aqueuse de ces gemmes, ainsi que de quelques autres échantillons d'essence provenant de la distillation industrielle de gemmes similaires, a donné les résultats suivants:

| Echantillon<br>n° | Densité à 25° | Indice de réfraction<br>$n_D$ à 25° | Pouvoir rotatoire<br>( $\alpha$ ) <sub>D</sub> |
|-------------------|---------------|-------------------------------------|--|
| 1                 | 0,8556        | 1,4640                              | +46°,9   |
| 2                 | 0,8568        | 1,4652                              | +46°,7   |
| 3                 | 0,8556        | 1,4638                              | +46°,6   |
| 4                 | 0,8557        | 1,4644                              | +47°,8   |
| 5                 | 0,8561        | 1,4643                              | +47°,4   |
| 6                 | 0,8548        | 1,4642                              | +47°,6   |
| 7                 | 0,8546        | 1,4638                              | +47°,3   |
| 8                 | 0,8549        | 1,4641                              | +47°,6   |
| 9                 | 0,8553        | 1,4645                              | +46°,9   |
| 10                | 0,8552        | 1,4639                              | +47°,6   |
| 11                | 0,8562        | 1,4648                              | +46°,5   |

Ces résultats confirment, comme on le voit, ceux que nous avons donnés en 1909: ces essences sont fortement dextrogyres et diffèrent peu les unes des autres. Au fractionnement, elles se montrent très homogènes: sous la pression atmosphérique normale, la majeure partie passe entre 154° et 156°, et les fractions recueillies dans cet intervalle, pendant la distillation d'une même essence, possèdent des constantes physiques à peu près identiques. Voici la valeur de ces constantes pour celles des essences décrites ci dessus dont le fractionnement a été opéré.

| Echant.<br>n° | $d_{25}^{\circ}$ | $n_D$ à $25^{\circ}$ | $(\alpha)_D$ |
|---------------|------------------|----------------------|--------------|
| 1             | 0,8543           | 1,4636               | +48°,1       |
| 3             | 0,8547           | 1,4633               | +47°,4       |
| 4             | 0,8548           | 1,4638               | +48°,7       |
| 5             | 0,8550           | 1,4638               | +48°,7       |
| 6             | 0,8545           | 1,4639               | +48°,5       |
| 7             | 0,8541           | 1,4636               | +47°,8       |
| 8             | 0,8547           | 1,4637               | +47°,9       |
| 9             | 0,8541           | 1,4639               | +47°,8       |
| 10            | 0,8542           | 1,4634               | +48°,4       |
| 11            | 0,8545           | 1,4638               | +48°,0       |

Comme nous l'avons montré en 1909<sup>1</sup>, ces données correspondent sensiblement à celles du pinène pur, pour lequel on a (mesures faites sur des échantillons de pinène inactif régénéré de son nitrosochlorure):

| Auteur                          | Ebullition sous 760 mm. | $d_{25}^{\circ}$ | $n_D$ à $25^{\circ}$ |
|---------------------------------|-------------------------|------------------|----------------------|
| Wallach <sup>2</sup> . . . . .  | 155° -156°              | 0,8540           | 1,4635               |
| Schimmel <sup>3</sup> . . . . . | 154°,5-155°             | 0,8554           | 1,4639               |

et pour lequel le pouvoir rotatoire le plus fort observé dans des échantillons gauches a été<sup>4</sup>

$$(\alpha)_D = -48^{\circ},63,$$

nombre presque indentique, au signe près, au maximum (+48°,7) obtenu par nous dans le fractionnement de nos échantillons 4 et 5.

Ces résultats sont d'accord avec ceux qu'a récemment obtenus

<sup>1</sup> Loc. cit., p. 932-933.

<sup>2</sup> Wallach, Liebigs Annalen, t. 258, p. 344; 1890. L'indice, mesuré à  $21^{\circ}$ , a été ramené à  $25^{\circ}$  au moyen du coefficient de température 0,0005.

<sup>3</sup> Gildemeister, Die Aetherische Oele, 2° Auflage, t. 1, p. 308; 1910. La densité et l'indice, mesurés à  $15^{\circ}$  et  $20^{\circ}$ , ont été ramenés à  $25^{\circ}$  au moyen des coefficients de température 0,0008 et 0,0005.

<sup>4</sup> Smith, in Bericht von Schimmel & Co., avril 1899, p. 24.

M. Darmois,<sup>1</sup> au cours de ses recherches sur la dispersion rotatoire des corps actifs.

Partant de ce principe, conséquence de la règle de Biot, que "la caractéristique d'une espèce chimique est, non pas le pouvoir rotatoire pour telle ou telle couleur, mais la dispersion rotatoire,"<sup>2</sup> M. Darmois a déterminé la dispersion rotatoire du pinène pour les principales raies du spectre du mercure, c'est à dire les rapports de la rotation observée pour chacune de ces raies (raie jaune,  $\lambda = 578\mu\mu$ ; raie verte,  $\lambda = 546\mu\mu$ ; raie bleue,  $\lambda = 436\mu\mu$ ) à la rotation donnée, toutes choses égales d'ailleurs, par la raie jaune du sodium ( $\lambda = 589\mu\mu$ ). Il a obtenu ainsi, au moyen de pinène pur extrait de l'essence de pin d'Alep, les nombres suivants,<sup>3</sup> qui caractérisent le pinène, indépendamment de son pouvoir rotatoire, aussi bien que son point d'ébullition, sa densité ou son indice de réfraction:

|                         |                       |             |             |             |
|-------------------------|-----------------------|-------------|-------------|-------------|
|                         | $\lambda = 589\mu\mu$ | $578\mu\mu$ | $546\mu\mu$ | $436\mu\mu$ |
| Dispersion rotatoire: 1 | 1,043                 | 1,185       | 2,017       |             |

Nous avons déterminé, relativement aux mêmes lumières monochromatiques, la dispersion rotatoire de quelques uns de nos échantillons d'essence de pin d'Alep; le tableau suivant donne les résultats de ces mesures.

| Echant. n° | ( $\alpha$ ) <sub>D</sub> | $\lambda = 589\mu\mu$ | $578\mu\mu$ | $546\mu\mu$ | $436\mu\mu$ |
|------------|---------------------------|-----------------------|-------------|-------------|-------------|
| 4          | +47°,8                    | 1                     | 1,042       | 1,184       | 2,016       |
| 5          | +47°,4                    | 1                     | 1,042       | 1,183       | 2,006       |
| 6          | +47°,6                    | 1                     | 1,046       | 1,188       | 2,016       |
| 7          | +47°,3                    | 1                     | 1,044       | 1,182       | 2,015       |
| 8          | +47°,6                    | 1                     | 1,040       | 1,181       | 2,004       |
| 10         | +47°,6                    | 1                     | 1,045       | 1,188       | 2,010       |
| 11         | +46°,5                    | 1                     | 1,044       | 1,185       | 2,009       |

De ces résultats comme de ceux qui précèdent, il paraît légitime de conclure que l'essence de térébenthine extraite par distillation aqueuse de la gemme de Pin d'Alep est constituée presque exclusivement par du pinène droit.

<sup>1</sup> Darmois, Thèse Paris 1910, p. 63.

<sup>2</sup> Loc. cit., p. 45.

<sup>3</sup> Loc. cit., p. 66.



II—Nous avons eu entre les mains deux échantillons de gomme provenant du *Pinus Massoniana* Sieb. & Zucc., arbre qui croît sur les hauts plateaux de l'Inde anglaise et de la Birmanie. La composition immédiate de ces deux échantillons était la suivante:

| Echant. n° | Essence | Produit sec. | Impuretés solides, eau et perte. |
|------------|---------|--------------|----------------------------------|
| 1          | 20,3%   | 78,1%        | 1,6%                             |
| 2          | 22,1    | 77,8         | 0,1                              |

Le premier, récolté dans d'assez mauvaises conditions, paraissait assez altéré; le deuxième au contraire paraissait récolté avec beaucoup de soin: il ne contenait sensiblement pas d'eau ni d'impuretés solides.

L'essence retirée de ces gommés par distillation aqueuse présentait les caractères suivants:

| Echant. n° | $d_{20}^{\circ}$ | $n_D$ à 25° | $(\alpha)_D$ | Dispersion rotatoire  |             |             |             |
|------------|------------------|-------------|--------------|-----------------------|-------------|-------------|-------------|
|            |                  |             |              | $\lambda = 589\mu\mu$ | $578\mu\mu$ | $546\mu\mu$ | $436\mu\mu$ |
| 1          | 0,8538           | 1,4645      | +36°,4       | 1                     | "           | "           | "           |
| 2          | 0,8532           | 1,4650      | +31,6        | 1                     | 1,040       | 1,180       | 2,021       |
| 3          | 0,8541           | 1,4647      | +42,4        | 1                     | 1,042       | 1,180       | "           |

Les échantillons 1 et 2 ont été recueillis au cours de la distillation de la gomme n° 1; l'échantillon n° 3 est le produit total de celle de la gomme n° 2. On voit que ces essences, très comparables en ce qui concerne la densité, l'indice de réfraction et la dispersion rotatoire, diffèrent cependant notablement par la valeur de leur pouvoir rotatoire.

Soumis au fractionnement, ces échantillons se sont montrés très homogènes: sous la pression atmosphérique normale, la majeure partie passe entre 154° et 156°, et les fractions recueillies dans cet intervalle diffèrent fort peu les unes des autres en ce qui concerne la densité et l'indice, comme le montre le tableau suivant:

|          |   | Echant. n° 1     |             | Echant. n° 2     |             | Echant. n° 3     |             |
|----------|---|------------------|-------------|------------------|-------------|------------------|-------------|
|          |   | $d_{25}^{\circ}$ | $n_D$ à 25° | $d_{25}^{\circ}$ | $n_D$ à 25° | $d_{25}^{\circ}$ | $n_D$ à 25° |
| Fraction | 1 | 0,8539           | 1,4640      | 0,8536           | 1,4643      | 0,8542           | 1,4640      |
|          | 2 | 0,8539           | 1,4640      | 0,8537           | 1,4643      | 0,8542           | 1,4641      |
|          | 3 | 0,8541           | 1,4641      | 0,8538           | 1,4644      | 0,8543           | 1,4642      |
|          | 4 | 0,8537           | 1,4642      | 0,8535           | 1,4648      | 0,8541           | 1,4646      |
| Residu   |   | 0,8530           | 1,4658      | 0,8530           | 1,4669      | 0,8555           | 1,4661      |

En revanche, la rotation (mesurée dans un tube de 100 millim. et pour la raie D) subit une décroissance sensible de la première fraction à la cinquième: la densité des fractions étant très voisine, leur pouvoir rotatoire décroît évidemment de la même façon. Mais si l'on mesure, comme nous l'avons fait pour l'échantillon n° 3, les rotations pour les raies jaune et verte du mercure, on trouve pour les dispersions correspondantes des valeurs sensiblement constantes:

|            | Echant n°1<br>$\alpha_D$ | Echant. n°2<br>$\alpha_D$ | Echant. n°3<br>$\alpha_D$ | $\lambda = 589 \mu\mu$ | $578 \mu\mu$ | $546 \mu\mu$ |
|------------|--------------------------|---------------------------|---------------------------|------------------------|--------------|--------------|
| Fraction 1 | +35°,00                  | +33°,00                   | +38°,27                   | 1                      | 1,043        | 1,184        |
| 2          | +34,37                   | +31,90                    | +37,87                    | 1                      | 1,042        | 1,181        |
| 3          | +33,10                   | +30,10                    | +37,43                    | 1                      | 1,038        | 1,180        |
| 4          | +30,90                   | +26,81                    | +36,33                    | 1                      | 1,041        | 1,181        |
| Résidu     | +20,76                   | +12,57                    | +31,30                    | 1                      | 1,045        | 1,188        |

Ces dispersions, comme celles des essences elles-mêmes, se trouvent être sensiblement égales à celles du pinène pur, qui comme nous l'avons vu plus haut, donne pour les mêmes radiations les valeurs.

$$1 \quad 1,043 \quad 1,185.$$

Comme on vient de voir d'autre part que le point d'ébullition, la densité et l'indice de réfraction des fractions distillées s'écartent peu de ceux du pinène pur, qui ont été donnés plus haut, on est

en droit d'en conclure que l'essence de térébenthine extraite par distillation aqueuse de la gomme du *Pinus Massoniana* est constituée presque exclusivement par du pinène (pinène droit mélangé d'un peu de pinène gauche, ou pinène droit partiellement racémisé).







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OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

SECTION VIa.  
STARCH, CELLULOSE AND PAPER



458923-7  
7.3.47

VOL. XIII

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W. A. NIVLING, Ph.C.

L. A. OLNEY, A.C., M.S.

F. P. VEITCH, M.S.

and the Sectional Executive Committee

# VOLUME 13

## SECTION VIa.—STARCH, CELLULOSE AND PAPER

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## THE EFFECT OF ACIDITY AND TIME IN THE ROASTING OF DEXTRINES

BY H. F. BAUER

*Waukegan, Illinois*

A series of experiments were undertaken with a view to ascertaining what effect the degree of acidity and the time of roasting had upon the resultant dextrine. An ordinary powdered corn starch of the following composition was used in all of these experiments:

|                               |       |
|-------------------------------|-------|
| Moisture                      | 10.48 |
| Ash                           | .12   |
| Protein                       | .44   |
| Fiber                         | .21   |
| Watersoluble                  | .48   |
| Starch by difference          | 88.75 |
| Acidity—cc. n/10 per 100 grs. | —18   |
| Acidity—boiled                | —20   |

The starch is placed in pans holding about 15 pounds each and put into kilns heated with steam coils to about 300° F. There are about twenty-six tiers of steam coils per kiln.

The methods used in obtaining my analytical data were the following:

1. *Watersoluble at 70° F.* Two grams dextrine were shaken for one hour with 50 cc. water in a 100 cc. graduated flask, which was then filled to the mark, shaken and allowed to stand for one hour, then filtered. 25 cc. of the clear filtrate were evaporated to dryness on steam bath in a tared glass evaporating dish and then dried in both at a temperature of 215° F. for one hour, cooled and weighed.

2. *Acidity expressed in number of n/10 cc.*

a. *Direct acidity:* One gram dextrine was distributed in 200 cc. hot water and titrated with n/10 NaOH using phenolphthalein as indicator.

b. *Acidity of soluble*: 50 cc. of the watersoluble representing one gram of the dextrine were mixed with 500 cc. water and titrated with  $n/10$  NaOH and phenolphthalein as indicator.

3. *Reducing Sugars* were determined volumetrically with Fehlings solution, which was so standardized that 5 cc. equalled .025 gram glucose. Five grams dextrine were shaken with water in a 200 cc. graduated flask, filled to the mark and allowed to stand for 4 hours with frequent shaking. Five cc. of Fehlings solution diluted with 10 cc. water was then titrated with the clear filtrate representing 2.5 grams dextrine in 100 cc. until the drop test (potassium ferrocyanide and acetic acid) showed complete reduction.

## EXPERIMENT 1

## 1000 LBS. OF STARCH WITHOUT ADDITION OF ANY ACID

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. $1/10N$ NaOH | Acidity of Soluble cc. $1/10 N$ NaOH | Water Soluble | Water Insoluble | Reducing Sugars as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|---------------------------------|--------------------------------------|---------------|-----------------|----------------------------|-------------------------|
| 1        | 308°F.        | 4             | 20                              | 20                                   | .28           | 99.72           |                            | Starchy                 |
| 2        | 311           | 8             | 30                              | 22                                   | 3.3           | 96.7            |                            | Starchy                 |
| 3        | 312           | 12            | 40                              | 20                                   | 13.2          | 86.8            |                            | Starchy                 |
| 4        | 290           | 16            | 40                              | 20                                   | 20.6          | 79.4            |                            | Starchy                 |
| 5        | 310           | 20            | 40                              | 20                                   | 37.2          | 62.8            | Trace                      | Starchy                 |
| 6        | 310           | 24            | 40                              | 20                                   | 41.4          | 58.6            |                            | Starchy                 |
| 7        | 310           | 28            | 50                              | 35                                   | 45.9          | 54.1            |                            | Starchy                 |
| 8        | 310           | 32            | 50                              | 40                                   | 48.1          | 51.9            |                            | Starchy                 |
| 9        | 312           | 36            | 55                              | 40                                   | 72.6          | 27.4            |                            | Gummy                   |
| 10       | 300           | 40            | 60                              | 55                                   | 75.2          | 24.8            | .84                        | Gummy                   |
| 11       | 298           | 44            | 60                              | 60                                   | 79.0          | 21.0            |                            | Gummy                   |
| 12       | 300           | 48            | 60                              | 60                                   | 77.6          | 22.4            |                            | Gummy                   |
| 13       | 308           | 52            | 70                              | 60                                   | 78.1          | 21.9            |                            | Gummy                   |
| 14       | 294           | 56            | 55                              | 60                                   | 83.2          | 16.8            |                            | Gummy                   |
| 15       | 290           | 60            | 60                              | 75                                   | 82.5          | 17.5            | 1.35                       | Gummy                   |
| 16       | 292           | 64            | 60                              | 75                                   | 77.8          | 22.2            |                            | Gummy                   |
| 17       | 294           | 68            | 60                              | 60                                   | 81.3          | 18.7            |                            | Gummy                   |
| 18       | 302           | 72            | 60                              | 70                                   | 81.7          | 18.3            |                            | Gummy                   |
| 19       | 303           | 76            | 60                              | 75                                   | 84.0          | 16.0            |                            | Gummy                   |
| 20       | 310           | 80            | 60                              | 80                                   | 82.7          | 17.3            | 1.47                       | Gummy                   |
| 21       | 307           | 84            | 60                              | 80                                   | 84.8          | 15.2            |                            | Gummy                   |



## EXPERIMENT I

100 LBS. OF STARCH WITHOUT ADDITION OF ANY KIND

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 NaOH | Water Soluble | Water Insoluble | Reducing Sugars as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|--------------------------------|----------------------------------|---------------|-----------------|----------------------------|-------------------------|
| 22       | 315           | 88            | 70                             | 80                               | 86.2          | 13.8            |                            | Gummy                   |
| 23       | 315           | 92            | 70                             | 80                               | 90.2          | 9.8             |                            | Gummy                   |
| 24       | 306           | 96            | 70                             | 100                              | 92.5          | 7.5             |                            | Gummy                   |
| 25       | 310           | 100           | 60                             | 110                              | 95.8          | 4.2             | 1.92                       | Gummy                   |
| 26       | 312           | 104           | 50                             | 80                               | 98.2          | 1.8             |                            | Gummy                   |
| 27       | 312           | 108           | 80                             | 100                              | 99.1          | .9              |                            | Gummy                   |
| 28       | 312           | 112           | 70                             | 100                              | 98.8          | 1.2             |                            | Gummy                   |
| 29       | 313           | 116           | 80                             | 100                              | 96.5          | 3.5             |                            | Gummy                   |
| 30       | 303           | 120           | 80                             | 100                              | 97.9          | 2.1             | 2.00                       | Gummy                   |
| 31       | 313           | 124           | 80                             | 100                              | 98.2          | 1.8             |                            | Gummy                   |
| 32       | 312           | 128           | 80                             | 90                               | 95.8          | 4.2             |                            | Gummy                   |
| 33       | 310           | 132           | 80                             | 80                               | 94.1          | 5.9             |                            | Gummy                   |
| 34       | 312           | 136           | 80                             | 95                               | 93.4          | 6.6             | Very                       | Gummy                   |
| 35       | 304           | 140           | 100                            | 100                              | 92.5          | 7.5             | 2.43                       | Gummy                   |
| 36       | 306           | 144           | 100                            | 110                              | 92.2          | 7.8             |                            | Gummy                   |
| 37       | 312           | 148           | 90                             | 95                               | 91.2          | 8.8             |                            | Gummy                   |
| 38       | 313           | 152           | 90                             | 100                              | 84.3          | 15.7            |                            | Gummy                   |
| 39       | 310           | 156           | 100                            | 100                              | 80.3          | 19.7            |                            | Gummy                   |
| 40       | 310           | 160           | 100                            | 90                               | 76.5          | 23.5            | 2.38                       | Gummy                   |
| 41       | 306           | 164           | 100                            | 95                               | 75.6          | 24.5            |                            | Gummy                   |
| 42       | 310           | 168           | 90                             | 100                              | 74.2          | 25.8            |                            | Gummy                   |
| 43       | 311           | 172           | 90                             | 100                              | 76.0          | 24.0            |                            | Gummy                   |
| 44       | 310           | 176           | 100                            | 120                              | 69.6          | 30.4            |                            | Gummy                   |
| 45       | 312           | 180           | 100                            | 100                              | 69.0          | 31.0            | 2.27                       | Gummy                   |
| 46       | 311           | 184           | 110                            | 100                              | 65.8          | 34.2            |                            | Gummy                   |
| 47       | 312           | 188           | 100                            | 110                              | 65.7          | 34.3            |                            | Gummy                   |
| 48       | 312           | 192           | 100                            | 120                              | 66.0          | 34.0            |                            | Gummy                   |
| 49       | 312           | 196           | 110                            | 110                              | 65.1          | 34.8            |                            | Gummy                   |
| 50       | 312           | 200           | 80                             | 100                              | 65.8          | 34.2            | 2.27                       | Gummy                   |
| 51       | 312           | 204           | 110                            | 120                              | 65.2          | 34.8            |                            | Gummy                   |
| 52       | 310           | 208           | 110                            | 120                              | 63.6          | 36.4            |                            | Gummy                   |
| 53       | 310           | 212           | 120                            | 120                              | 64.7          | 35.3            |                            | Gummy                   |
| 54       | 310           | 216           | 110                            | 110                              | 65.0          | 35.0            |                            | Gummy                   |
| 55       | 310           | 220           | 110                            | 120                              | 64.8          | 35.2            | 2.08                       | Gummy                   |

## EXPERIMENT 1

## 100 LBS. OF STARCH WITHOUT ADDITION OF ANY ACID

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 N NaOH | Water Soluble | Water Insoluble | Reducing Sugars as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|--------------------------------|------------------------------------|---------------|-----------------|----------------------------|-------------------------|
| 56       | 310           | 224           | 110                            | 120                                | 62.6          | 37.4            |                            | Gummy                   |
| 57       | 311           | 228           | 120                            | 120                                | 61.0          | 39.0            |                            | Gummy                   |
| 58       | 310           | 232           | 120                            | 120                                | 50.4          | 49.6            |                            | Gummy                   |
| 59       | 312           | 236           | 120                            | 120                                | 50.2          | 49.8            |                            | Gummy                   |
| 60       | 310           | 240           | 120                            | 120                                | 50.0          | 50.0            | 1.96                       | Gummy                   |
| 61       | 310           | 244           | 120                            | 120                                | 49.6          | 50.4            |                            | Gummy                   |
| 62       | 312           | 248           | 120                            | 120                                | 49.5          | 50.5            |                            | Gummy                   |
| 63       | 310           | 252           | 120                            | 120                                | 48.9          | 51.1            |                            | Gummy                   |
| 64       | 310           | 256           | 120                            | 120                                | 48.5          | 51.5            |                            | Gummy                   |
| 65       | 310           | 260           | 120                            | 120                                | 47.0          | 53.0            | 1.75                       | Gummy                   |

## EXPERIMENT 2

## 1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, FOUR LBS. OF A 38° BE, ACID DILUTED TO 12° BE

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 N NaOH | Water Soluble | Water Insoluble | Reducing Sugars as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|--------------------------------|------------------------------------|---------------|-----------------|----------------------------|-------------------------|
| 1        | 298°F.        | 2             | 55.0                           | 75.0                               | 73.6          | 26.4            |                            | Starchy                 |
| 2        | 297           | 4             | 55.0                           | 75.5                               | 96.8          | 4.0             |                            | Starchy                 |
| 3        | 300           | 6             | 70.0                           | 76.0                               | 98.0          | 2.0             |                            | Starchy                 |
| 4        | 298           | 8             | 85.0                           | 78.5                               | 99.2          | .8              |                            | None                    |
| 5        | 303           | 10            | 85.0                           | 80.4                               | 98.8          | 1.2             | 5.08                       | Gummy                   |
| 6        | 298           | 12            | 95.0                           | 80.4                               | 98.4          | 1.6             |                            | Gummy                   |
| 7        | 310           | 14            | 105.0                          | 80.4                               | 90.0          | 10.0            |                            | Gummy                   |
| 8        | 300           | 16            | 100.0                          | 90.0                               | 90.0          | 10.0            |                            | Gummy                   |
| 9        | 302           | 18            | 70.0                           | 90.5                               | 89.6          | 10.4            |                            | Gummy                   |
| 10       | 298           | 20            | 70.0                           | 96.4                               | 90.4          | 9.6             | 3.72                       | Gummy                   |
| 11       | 297           | 22            | 75.0                           | 96.4                               | 86.0          | 14.0            |                            | Gummy                   |
| 12       | 297           | 24            | 67.5                           | 95.6                               | 86.0          | 14.0            |                            | Gummy                   |
| 13       | 299           | 26            | 67.5                           | 98.5                               | 88.8          | 11.2            | Very                       | Gummy                   |
| 14       | 304           | 28            | 79.5                           | 90.5                               | 86.8          | 13.2            |                            | Gummy                   |
| 15       | 295           | 30            | 79.5                           | 112.0                              | 86.4          | 13.6            | 3.25                       | Gummy                   |
| 16       | 293           | 32            | 82.5                           | 110.5                              | 86.0          | 14.0            |                            | Gummy                   |
| 17       | 302           | 34            | 82.5                           | 112.0                              | 84.4          | 15.6            |                            | Gummy                   |
| 18       | 299           | 36            | 75.0                           | 120.0                              | 85.6          | 14.4            |                            | Gummy                   |

## EXPERIMENT 2

1000 LBS. OF STARCH SOLIDIFIED WITH NITRIC ACID, FOUR LBS. OF  
A 38° BE, ACID DILUTED TO 12° BE

| Test No.        | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 NaOH | Water Soluble | Water Insoluble | Reducing Sugars as Glucose | Appearance of Insoluble |
|-----------------|---------------|---------------|--------------------------------|----------------------------------|---------------|-----------------|----------------------------|-------------------------|
| 19              | 301           | 38            | 80.0                           | 125.0                            | 82.4          | 17.6            |                            | Gummy                   |
| 20              | 304           | 40            | 75.0                           | 144.0                            | 82.0          | 18.0            | 2.89                       | Gummy                   |
| 21              | 302           | 42            | 75.0                           | 145.0                            | 80.8          | 19.2            |                            | Gummy                   |
| 22              | 300           | 44            | 90.0                           | 145.0                            | 80.0          | 20.0            |                            | Gummy                   |
| 23              | 304           | 46            | 90.0                           | 150.0                            | 78.4          | 21.6            |                            | Gummy                   |
| 24              | 300           | 48            | 90.2                           | 150.0                            | 75.2          | 24.6            |                            | Gummy                   |
| 25              | 302           | 50            | 90.5                           | 155.0                            | 76.4          | 23.6            | 2.77                       | Gummy                   |
| 26              | 300           | 52            | 90.0                           | 155.0                            | 74.2          | 25.8            |                            | Gummy                   |
| 27              | 296           | 54            | 90.0                           | 155.5                            | 74.2          | 25.8            |                            | Gummy                   |
| 28              | 302           | 56            | 90.2                           | 160.0                            | 74.1          | 25.9            |                            | Gummy                   |
| 29              | 298           | 58            | 90.5                           | 160.0                            | 75.6          | 24.4            |                            | Gummy                   |
| 30              | 298           | 60            | 105.0                          | 160.0                            | 75.0          | 25.0            | 2.67                       | Gummy                   |
| 31              | 300           | 62            | 100.0                          | 160.0                            | 74.7          | 25.3            |                            | Gummy                   |
| 32              | 308           | 64            | 80.0                           | 160.5                            | 74.7          | 25.3            |                            | Gummy                   |
| 33              | 302           | 66            | 65.0                           | 160.0                            | 74.5          | 25.5            |                            | Gummy                   |
| 34              | 297           | 68            | 70.0                           | 160.5                            | 74.0          | 26.0            |                            | Gummy                   |
| 35              | 304           | 70            | 80.0                           | 160.0                            | 73.9          | 26.1            | 2.56                       | Gummy                   |
| 36              | 305           | 72            | 85.0                           | 160.0                            | 73.0          | 27.0            |                            | Gummy                   |
| 37              | 301           | 74            | 80.0                           | 160.5                            | 72.9          | 27.1            |                            | Gummy                   |
| 38              | 301           | 76            | 75.0                           | 170.0                            | 72.4          | 27.6            |                            | Gummy                   |
| 39              | 300           | 78            | 90.0                           | 160.0                            | 72.4          | 27.6            |                            | Gummy                   |
| 40              | 299           | 80            | 85.0                           | 160.5                            | 72.1          | 27.9            | 2.39                       | Gummy                   |
| 41 <sup>1</sup> | 330           | 82            | 85.0                           | 160.5                            | 69.7          | 30.3            |                            | Gummy                   |
| 42              | 332           | 84            | 80.0                           | 160.5                            | 68.7          | 31.3            |                            | Gummy                   |
| 43              | 340           | 86            | 90.0                           | 160.0                            | 66.0          | 34.0            |                            | Gummy                   |
| 44              | 340           | 88            | 105.0                          | 160.0                            | 59.5          | 40.5            |                            | Gummy                   |
| 45              | 340           | 90            | 120.0                          | 160.0                            | 52.0          | 48.0            | 2.34                       | Gummy                   |
| 46              | 336           | 92            | 125.0                          | 160.0                            | 44.2          | 55.8            |                            | Gummy                   |
| 47              | 340           | 94            | 120.0                          | 160.0                            | 40.0          | 60.0            |                            | Gummy                   |
| 48              | 339           | 96            | 125.0                          | 160.5                            | 37.9          | 62.1            |                            | Gummy                   |
| 49              | 336           | 98            | 130.0                          | 160.5                            | 36.7          | 63.3            |                            | Gummy                   |
| 50              | 340           | 100           | 140.0                          | 160.5                            | 35.2          | 64.8            | 2.18                       | Getting Granular        |

<sup>1</sup>Temperature raised about 30° F. at this point.

## EXPERIMENT 2

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, FOUR LBS. OF  
A 38° BE, ACID DILUTED TO 12° BE

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 NaOH | Water Soluble | Water Insoluble | Reducing Sugars as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|--------------------------------|----------------------------------|---------------|-----------------|----------------------------|-------------------------|
| 51       | 340           | 102           | 140.0                          | 160.5                            | 34.9          | 65.1            |                            | Getting Granular        |
| 52       | 341           | 104           | 120.0                          | 170.0                            | 31.0          | 69.0            |                            | Getting Granular        |
| 53       | 339           | 106           | 140.0                          | 160.0                            | 29.5          | 70.5            |                            | Getting Granular        |
| 54       | 338           | 108           | 160.0                          | 160.0                            | 30.2          | 69.8            |                            | Granular                |
| 55       | 336           | 110           | 120.0                          | 160.5                            | 28.3          | 71.7            | 1.89                       | Granular                |
| 56       | 339           | 112           | 175.0                          | 160.0                            | 27.3          | 72.7            |                            | Granular                |
| 57       | 336           | 114           | 170.0                          | 160.5                            | 26.0          | 74.0            |                            | Granular                |
| 58       | 339           | 116           | 175.0                          | 160.0                            | 25.5          | 74.5            |                            | Granular                |
| 59       | 340           |               | 175.0                          | 160.0                            | 25.0          | 75.0            |                            | Granular                |
| 60       | 340           | 120           | 170.0                          | 155.0                            | 24.8          | 75.2            | 1.64                       | Granular                |
| 61       | 340           | 122           | 170.0                          | 165.0                            | 23.5          | 76.5            |                            | Granular                |
| 62       | 342           | 124           | 170.0                          | 165.0                            | 21.0          | 79.0            |                            | Granular                |
| 63       | 340           | 126           | 170.0                          | 160.0                            | 20.5          | 79.5            |                            | Granular                |
| 64       | 339           | 128           | 170.0                          | 160.0                            | 20.0          | 80.0            |                            | Granular                |
| 65       | 340           | 130           | 175.0                          | 160.5                            | 19.8          | 80.2            | 1.46                       | Granular                |

## EXPERIMENT 3

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, EIGHT LBS. OF A  
38° BE, ACID DILUTED TO 12° BE

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 NaOH | Water Soluble | Water Insoluble | Reducing Sugars as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|--------------------------------|----------------------------------|---------------|-----------------|----------------------------|-------------------------|
| 1        | 300°F.        | 1             | 90.0                           | 85.0                             | 65.8          | 34.2            |                            | Starchy                 |
| 2        | 298           | 2             | 85.0                           | 125.0                            | 86.9          | 13.2            |                            | Starchy                 |
| 3        | 297           | 4             | 85.0                           | 145.0                            | 99.7          | .3              |                            | None                    |
| 4        | 300           | 6             | 100.0                          | 200.0                            | 99.5          | .5              |                            | None                    |
| 5        | 302           | 8             | 105.0                          | 200.0                            | 96.8          | 4.2             | 5.10                       | Gummy                   |
| 6        | 310           | 10            | 110.0                          | 200.0                            | 84.1          | 15.9            |                            | Gummy                   |
| 7        | 304           | 12            | 120.0                          | 200.0                            | 78.1          | 21.9            |                            | Gummy                   |
| 8        | 312           | 14            | 125.0                          | 200.0                            | 73.5          | 26.5            |                            | Gummy                   |
| 9        | 302           | 16            | 135.0                          | 200.0                            | 72.0          | 28.0            |                            | Gummy                   |
| 10       | 300           | 18            | 135.0                          | 200.0                            | 71.8          | 28.2            | 3.56                       | Gummy                   |
| 11       | 310           | 20            | 135.0                          | 200.0                            | 67.8          | 32.2            |                            | Gummy                   |
| 12       | 297           | 22            | 135.0                          | 200.0                            | 70.0          | 30.0            |                            | Gummy                   |

## EXPERIMENT 3

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, EIGHT LBS. OF  
A 38° BE, ACID DILUTED TO 12° BE

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 N NaOH | Water Soluble | Water Insoluble | Reducing Sugars as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|--------------------------------|------------------------------------|---------------|-----------------|----------------------------|-------------------------|
| 13       | 300           | 24            | 140.0                          | 200.0                              | 66.8          | 33.2            |                            | Gummy                   |
| 14       | 308           | 26            | 140.0                          | 200.0                              | 64.9          | 35.1            | Very                       | Gummy                   |
| 15       | 300           | 28            | 180.0                          | 200.0                              | 63.7          | 36.3            | 2.78                       | Very Gummy              |
| 16       | 305           | 30            | 170.0                          | 200.0                              | 62.8          | 37.8            |                            | Gummy                   |
| 17       | 302           | 32            | 170.0                          | 200.0                              | 63.0          | 37.0            |                            | Gummy                   |
| 18       | 300           | 34            | 170.0                          | 200.0                              | 62.2          | 37.2            |                            | Gummy                   |
| 19       | 310           | 36            | 170.0                          | 200.0                              | 59.3          | 40.7            |                            | Gummy                   |
| 20       | 300           | 38            | 170.0                          | 195.0                              | 59.3          | 40.7            | 2.36                       | Gummy                   |
| 21       | 302           | 40            | 170.0                          | 180.0                              | 60.8          | 39.2            |                            | Gummy                   |
| 22       | 300           | 42            | 170.0                          | 160.0                              | 54.7          | 45.3            |                            | Gummy                   |
| 23       | 310           | 44            | 170.0                          | 180.0                              | 55.6          | 44.4            |                            | Gummy                   |
| 24       | 292           | 46            | 170.0                          | 180.0                              | 55.6          | 44.4            |                            | Gummy                   |
| 25       | 306           | 48            | 200.0                          | 180.0                              | 52.1          | 47.9            | 2.08                       | Gummy                   |
| 26       | 300           | 50            | 200.5                          | 170.0                              | 48.9          | 51.1            |                            | Gummy                   |
| 27       | 309           | 52            | 200.0                          | 170.0                              | 47.8          | 52.2            |                            | Gummy                   |
| 28       | 309           | 54            | 210.0                          | 180.0                              | 48.2          | 51.8            |                            | Gummy                   |
| 29       | 300           | 56            | 215.0                          | 165.0                              | 47.0          | 53.0            |                            | Gummy                   |
| 30       | 296           | 58            | 210.0                          | 165.0                              | 45.5          | 54.5            | 1.84                       | Gummy                   |
| 31       | 310           | 60            | 210.0                          | 165.0                              | 45.4          | 54.6            | Getting                    | Granular                |
| 32       | 302           | 62            | 205.0                          | 180.0                              | 42.2          | 57.8            | Getting                    | Granular                |
| 33       | 295           | 64            | 210.0                          | 180.0                              | 42.2          | 57.8            | Getting                    | Granular                |
| 34       | 310           | 66            | 200.0                          | 185.0                              | 41.5          | 58.5            | Getting                    | Granular                |
| 35       | 298           | 68            | 205.0                          | 185.0                              | 42.1          | 57.9            | 1.75                       | Getting Granular        |
| 36       | 290           | 70            | 210.0                          | 180.0                              | 42.2          | 57.8            | Getting                    | Granular                |
| 37       | 310           | 72            | 205.0                          | 170.0                              | 41.1          | 58.9            | Getting                    | Granular                |
| 38       | 300           | 74            | 195.0                          | 165.0                              | 39.1          | 60.9            | Getting                    | Granular                |
| 39       | 310           | 76            | 200.0                          | 175.0                              | 39.6          | 60.4            | Getting                    | Granular                |
| 40       | 300           | 78            | 200.0                          | 175.0                              | 38.3          | 61.7            | 1.69                       | Granular                |
| 41       | 302           | 80            | 200.0                          | 175.0                              | 37.2          | 62.8            |                            | Granular                |
| 42       | 312           | 82            | 200.0                          | 180.0                              | 36.4          | 63.6            |                            | Granular                |
| 43       | 300           | 84            | 200.0                          | 180.0                              | 36.6          | 63.4            |                            | Granular                |
| 44       | 296           | 86            | 200.0                          | 190.0                              | 36.0          | 64.0            |                            | Granular                |
| 45       | 306           | 88            | 200.0                          | 165.0                              | 35.6          | 64.4            | 1.65                       | Granular                |



## EXPERIMENT 3

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, EIGHT LBS. OF  
A 38 BE, ACID DILUTED TO 12° BE

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 N NaOH | Water Soluble | Water Insoluble | Reducing Sugar as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|--------------------------------|------------------------------------|---------------|-----------------|---------------------------|-------------------------|
| 46       | 312           | 90            | 200.0                          | 180.0                              | 34.6          | 65.4            |                           | Granular                |
| 47       | 300           | 92            | 200.0                          | 180.0                              | 33.9          | 66.1            |                           | Granular                |
| 48       | 290           | 94            | 200.0                          | 180.0                              | 32.4          | 67.6            |                           | Granular                |
| 49       | 306           | 96            | 200.0                          | 185.0                              | 33.0          | 67.0            |                           | Granular                |
| 50       | 300           | 98            | 195.0                          | 180.0                              | 33.8          | 66.2            | 1.61                      | Granular                |
| 51       | 306           | 100           | 200.0                          | 180.0                              | 33.2          | 66.8            |                           | Granular                |
| 52       | 302           | 102           | 200.0                          | 175.0                              | 33.8          | 66.2            |                           | Granular                |
| 53       | 310           | 104           | 205.0                          | 180.0                              | 33.0          | 67.0            |                           | Granular                |
| 54       | 300           | 106           | 205.0                          | 180.0                              | 30.8          | 69.2            |                           | Granular                |
| 55       | 308           | 108           | 210.0                          | 185.0                              | 30.8          | 69.2            | 1.60                      | Granular                |
| 56       | 302           | 110           | 205.0                          | 180.0                              | 30.9          | 69.1            |                           | Granular                |
| 57       | 302           | 112           | 215.0                          | 180.0                              | 30.8          | 69.2            |                           | Granular                |
| 58       | 310           | 114           | 210.0                          | 175.0                              | 29.8          | 70.2            |                           | Granular                |
| 59       | 310           | 116           | 210.0                          | 175.0                              | 30.1          | 69.9            |                           | Granular                |
| 60       | 300           | 118           | 210.0                          | 175.0                              | 30.2          | 69.8            | 1.56                      | Granular                |
| 61       | 300           | 120           | 210.0                          | 175.0                              | 30.0          | 70.0            |                           | Granular                |
| 62       | 302           | 122           | 210.0                          | 175.0                              | 29.8          | 70.2            |                           | Granular                |
| 63       | 305           | 124           | 210.0                          | 175.0                              | 28.1          | 71.9            |                           | Granular                |
| 64       | 306           | 126           | 210.0                          | 175.0                              | 27.6          | 72.4            |                           | Granular                |
| 65       | 305           | 128           | 210.0                          | 175.0                              | 27.0          | 73.0            | 1.42                      | Granular                |

## EXPERIMENT 4

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, TWELVE LBS. OF  
A 38° BE, ACID DILUTED TO 12° BE

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 N NaOH | Water Soluble | Water Insoluble | Reducing Sugar as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|--------------------------------|------------------------------------|---------------|-----------------|---------------------------|-------------------------|
| 1        | 285           | 1             | 110                            | 120                                | 45.5          | 54.5            |                           | Starchy                 |
| 2        | 295           | 2             | 100                            | 100                                | 67.5          | 32.5            |                           | Starchy                 |
| 3        | 285           | 3             | 100                            | 100                                | 88.2          | 11.8            |                           | Starchy                 |
| 4        | 286           | 4             | 90                             | 100                                | 92.0          | 8.0             |                           | Starchy                 |
| 5        | 304           | 6             | 90                             | 100                                | 98.6          | 1.4             | 7.14                      | None                    |
| 6        | 312           | 8             | 80                             | 120                                | 99.9          | .1              |                           | None                    |
| 7        | 312           | 10            | 120                            | 130                                | 98.4          | 1.6             |                           | None                    |

## EXPERIMENT 4

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, TWELVE LBS. OF  
A 38° BE, ACID DILUTED TO 12° BE

| Test.<br>No. | Temp.<br>of Kiln | Hours<br>in Kiln | Acidity<br>Direct cc.<br>1/10 N<br>NaOH | Acidity<br>of Soluble<br>cc. 1/10 N<br>NaOH | Water<br>Soluble | Water<br>Insoluble | Reducing<br>Sugar<br>as<br>Glucose | Appearance<br>of Insoluble |
|--------------|------------------|------------------|---|---|------------------|--------------------|------------------------------------|----------------------------|
| 8            | 311              | 12               | 120                                     | 130   | 96.3             | 3.7                |                                    | Gummy                      |
| 9            | 313              | 14               | 130                                     | 130   | 93.7             | 6.3                |                                    | Gummy                      |
| 10           | 313              | 16               | 120                                     | 140   | 94.0             | 6.0                | 4.54                               | Gummy                      |
| 11           | 308              | 18               | 120                                     | 140   | 92.5             | 7.5                |                                    | Gummy                      |
| 12           | 303              | 20               | 120                                     | 145   | 90.2             | 9.8                |                                    | Gummy                      |
| 13           | 298              | 22               | 140                                     | 160   | 90.1             | 9.9                |                                    | Gummy                      |
| 14           | 312              | 24               | 140                                     | 150   | 89.0             | 10.0               |                                    | Gummy                      |
| 15           | 295              | 26               | 150                                     | 160   | 87.2             | 12.8               | 4.49                               | Gummy                      |
| 16           | 308              | 28               | 150                                     | 160   | 87.5             | 12.5               |                                    | Gummy                      |
| 17           | 295              | 30               | 160                                     | 160   | 86.7             | 13.3               |                                    | Gummy                      |
| 18           | 290              | 32               | 160                                     | 170   | 82.2             | 17.8               |                                    | Gummy                      |
| 19           | 306              | 34               | 160                                     | 160   | 82.4             | 17.6               |                                    | Gummy                      |
| 20           | 310              | 36               | 170                                     | 160   | 80.4             | 19.6               | 4.44                               | Gummy                      |
| 21           | 304              | 38               | 180                                     | 150   | 79.8             | 20.2               |                                    | Gummy                      |
| 22           | 308              | 40               | 180                                     | 160   | 79.6             | 20.4               |                                    | Gummy                      |
| 23           | 290              | 42               | 160                                     | 150   | 77.3             | 22.7               |                                    | Gummy                      |
| 24           | 302              | 44               | 160                                     | 150   | 76.2             | 23.8               |                                    | Gummy                      |
| 25           | 315              | 46               | 180                                     | 150   | 72.7             | 27.3               | 4.20                               | Gummy                      |
| 26           | 310              | 48               | 180                                     | 150   | 73.0             | 27.0               |                                    | Gummy                      |
| 27           | 307              | 50               | 180                                     | 160   | 71.5             | 28.5               |                                    | Gummy                      |
| 28           | 301              | 52               | 180                                     | 160   | 70.2             | 29.8               | Very                               | Gummy                      |
| 29           | 300              | 54               | 180                                     | 150   | 64.9             | 35.1               | Very                               | Gummy                      |
| 30           | 306              | 56               | 180                                     | 155   | 61.1             | 38.9               | 3.73<br>Very<br>Gummy              |                            |
| 31           | 308              | 58               | 170                                     | 160   | 61.2             | 38.8               | Very                               | Gummy                      |
| 32           | 308              | 60               | 180                                     | 160   | 60.4             | 39.6               | Very                               | Gummy                      |
| 33           | 298              | 62               | 180                                     | 160   | 59.8             | 40.2               | Very                               | Gummy                      |
| 34           | 308              | 64               | 180                                     | 160   | 59.0             | 41.0               | Very                               | Gummy                      |
| 35           | 302              | 66               | 180                                     | 160   | 56.7             | 43.3               | 3.50<br>Very<br>Gummy              |                            |
| 36           | 306              | 68               | 180                                     | 160   | 57.0             | 43.0               | Very                               | Gummy                      |
| 37           | 296              | 70               | 180                                     | 160   | 53.2             | 46.8               | Very                               | Gummy                      |
| 38           | 310              | 72               | 180                                     | 160   | 52.1             | 47.9               | Very                               | Gummy                      |
| 39           | 310              | 74               | 180                                     | 160   | 49.5             | 50.5               | Very                               | Gummy                      |
| 40           | 306              | 76               | 180                                     | 160   | 49.1             | 50.9               | 3.39<br>Very<br>Gummy              |                            |

## EXPERIMENT 4

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, TWELVE LBS. OF  
A 38° BE, ACID DILUTED TO 12° BE

| Test No. | Temp. of Kiln | Hours in Kiln | Acidity Direct cc. 1/10 N NaOH | Acidity of Soluble cc. 1/10 N NaOH | Water Soluble | Water Insoluble | Reducing Sugar as Glucose | Appearance of Insoluble |
|----------|---------------|---------------|--------------------------------|------------------------------------|---------------|-----------------|---------------------------|-------------------------|
| 41       | 303           | 78            | 190                            | 160                                | 47.3          | 52.7            |                           | Very Gummy              |
| 42       | 301           | 80            | 190                            | 155                                | 49.2          | 50.8            |                           | Very Gummy              |
| 43       | 299           | 82            | 190                            | 155                                | 50.1          | 49.9            |                           | Very Gummy              |
| 44       | 302           | 84            | 190                            | 155                                | 50.3          | 49.7            |                           | Very Gummy              |
| 45       | 307           | 86            | 190                            | 155                                | 48.2          | 51.8            | 3.20                      | Getting Granular        |
| 46       | 309           | 88            | 190                            | 160                                | 47.8          | 52.2            |                           | Getting Granular        |
| 47       | 308           | 90            | 200                            | 160                                | 45.6          | 54.4            |                           | Getting Granular        |
| 48       | 297           | 92            | 190                            | 155                                | 43.7          | 56.3            |                           | Getting Granular        |
| 49       | 310           | 94            | 190                            | 155                                | 45.1          | 54.9            |                           | Getting Granular        |
| 50       | 312           | 96            | 200                            | 160                                | 43.8          | 56.2            | 3.12                      | Getting Granular        |
| 51       | 300           | 98            | 200                            | 155                                | 43.2          | 56.8            |                           | Getting Granular        |
| 52       | 300           | 100           | 195                            | 155                                | 42.7          | 57.3            |                           | Getting Granular        |
| 53       | 304           | 102           | 200                            | 160                                | 40.9          | 59.1            |                           | Getting Granular        |
| 54       | 309           | 104           | 200                            | 160                                | 40.4          | 59.6            |                           | Getting Granular        |
| 55       | 307           | 106           | 200                            | 150                                | 37.4          | 62.6            | 2.71                      | Getting Granular        |
| 56       | 305           | 108           | 200                            | 150                                | 36.4          | 63.6            |                           | Getting Granular        |
| 57       | 307           | 110           | 210                            | 155                                | 39.6          | 60.4            |                           | Getting Granular        |
| 58       | 310           | 112           | 210                            | 155                                | 40.4          | 59.6            |                           | Getting Granular        |
| 59       | 308           | 114           | 200                            | 155                                | 40.7          | 59.3            |                           | Getting Granular        |
| 60       | 310           | 116           | 200                            | 160                                | 39.7          | 60.3            | 2.50                      | Getting Granular        |
| 61       | 310           | 118           | 220                            | 155                                | 39.6          | 60.4            |                           | Granular                |
| 62       | 310           | 120           | 210                            | 155                                | 40.0          | 60.0            |                           | Granular                |
| 63       | 307           | 122           | 222                            | 155                                | 39.5          | 60.5            |                           | Granular                |
| 64       | 312           | 126           | 220                            | 160                                | 38.9          | 61.1            |                           | Granular                |
| 65       | 310           | 126           | 220                            | 165                                | 39.0          | 61.0            | 2.46                      | Granular                |

The temperatures in these experiments were not controlled as closely as might have been desired and the necessity of taking periodic samples caused a lowering of the temperature in the kiln of 10° to 15° F.; it took 15 to 20 minutes to raise to the initial temperature.

The most significant features shown in the experiments are the gradual and continuous rise in acidity and the increase of

soluble and reducing sugars to a certain point, followed by their gradual decline.

The fluctuations in the individual results can probably be attributed to an uneven operation in the kiln itself and a corresponding difference in the sample taken, due to a more rapid rate of conversion among the middle tiers of coils than at the top and bottom.





## PREPARATION OF CHEMICALLY PURE GLUCOSE FROM THE COMMERCIAL PRODUCTS

BY H. F. BAUER  
*Waukegan, Illinois*

When chemically pure glucose has to be prepared in the laboratory, Soxhlet's method is generally used. Soxhlet starts with cane sugar, which he inverts with concentrated hydrochloric acid, to which alcohol has been added. The glucose crystallizes out after about 10 days standing, when the mother liquor containing all of the frutase is removed on suction filter. Then the crystals are washed several times with 90% alcohol and finally recrystallized from methylalcohol.

The author has succeeded in making chemically pure glucose from the various commercial grades of sugars made by hydrolysis of starch. The three types used were "anhydrous sugar" (92.8 glucose), "80 sugar" (80.1% glucose), and "70 sugar" (71.2% glucose); all of these sugars contain a certain amount of moisture, mineral matter and dextrines. 80 and 70 sugars contain all the mother liquor, while the anhydrous sugar is nearly free from mother liquor, which has been removed by mechanical means. To remove this mother liquor from the raw glucose crystals a preliminary washing with methylalcohol is necessary. The sugars were ground up so finely that they could pass through a No. 20 mesh sieve; as 70 and 80 sugars contain a large amount of moisture, about 20% and 11% respectively, it is first necessary to cut these sugars in small pieces and dry them until most of the moisture content is driven out, then they can be easily ground.

The sugars are placed in a percolator with a cotton plug in its bottom covered with a small piece of filter paper; the percolator is so arranged that vacuum suction can be applied.

The sugars are now steeped with their weight of methylalcohol at ordinary room temperature, first for 12 hours when the alcohol

is removed by suction, then with a new portion of methylalcohol for 6 hours. For 70 and 80 sugars, a third washing must be applied.

The washed sugar crystals are dissolved in a small amount of distilled water, and when dissolved, alcohol is added. The solution is heated in steam bath, and then filtered to remove the insoluble impurities.

Amount of water and alcohol necessary for 100 grams of sugar taken in work:

|         | 70 Sugar | 80 Sugar | Anhydrous Sugar |
|---------|----------|----------|-----------------|
| Water   | 25cc.    | 30cc.    | 40cc.           |
| Alcohol | 100cc.   | 125cc.   | 140cc.          |

The solutions are now concentrated to syrupy consistency and methylalcohol added. For each 100 grams of sugar taken in work use:

|                     |       |
|---------------------|-------|
| For 70 sugar        | 50cc. |
| For 80 sugar        | 60cc. |
| For anhydrous sugar | 70cc. |

Let the solution stand for about one-half hour, until crystallization starts, then add again the same amount of methylalcohol and stir every 5 minutes to prevent hard incrustation of crystals on the dish; pour the mass into a percolator, let stand for 12 hours and remove mother liquor, using vacuum suction; steep for 15 minutes with 25cc. methylalcohol for each 100 grams of sugar taken in work; remove the alcohol, using suction; wash 3 times in this way. Dry the crystals in vacuum at a temperature not exceeding 90° C.

Such prepared glucose showed the following analysis:

|                         |             |
|-------------------------|-------------|
| Moisture                | none        |
| Ash                     | .005        |
| Nitrogenous matter      | none        |
| Dextrine                | none        |
| Specific rotatory power |             |
| [ $\alpha$ ] D 20 =     | 52.6        |
| Melting point           | 143-146° C. |

Anash-free glucose was obtained by recrystallization from methyl-alcohol.

I obtained the following yield from the three various types of commercial sugars taken in work:

|                 |     |
|-----------------|-----|
| Anhydrous sugar | 65% |
| 80 sugar        | 50% |
| 70 sugar        | 32% |



# THE INFLUENCE OF TEMPERATURE ON HYDRATION OF AND ABSORPTION OF ALKALI BY RE- GENERATED CELLULOSE

BY CLAYTON BEADLE AND HENRY P. STEVENS, M.A., PH.D.,  
F. I. C.

That cellulose has the power of absorbing<sup>1</sup> or condensing various dissolved substances when immersed in solutions of the same is known, although little has been done to investigate the mechanism of such reactions. It is well known that the power of hydration exercised by cellulose is largely influenced by the presence of caustic soda as well as by the "condition" or kind of cellulose submitted to the treatment.

Practically no work has been done upon the behaviour of any particular form of regenerated cellulose towards dissolved substances in promoting hydration and absorption. J. F. Briggs' investigations are interesting in this connection (*Der Papier Fabrikant* May 1910). On the other hand, work of a similar character has been done with cotton for the purpose of studying the question of mercerisation.

The object of this communication is primarily to describe work we have undertaken to determine the influence of temperature as affecting the behaviour of caustic soda of different concentrations towards a specific form of regenerated cellulose. The form of regenerated cellulose chosen by us was a monofil of uniform diameter made by the cuprammonium process in a factory under our supervision. This monofil had a denier of 360, it showed a breaking strain of 1.6 grams per denier and an elongation at break of 20% on the original length.

Lengths of the above in the form of small skeins weighing 0.200 grams were immersed in 20 cc. of the different solutions experimented with for periods of 30 minutes. The skeins were then taken out and weighed after the careful removal of any

<sup>1</sup>We are probably dealing with the phenomenon known as *adsorption*. We have not, however, used this term, as we are not satisfied that the action is entirely a physical one.



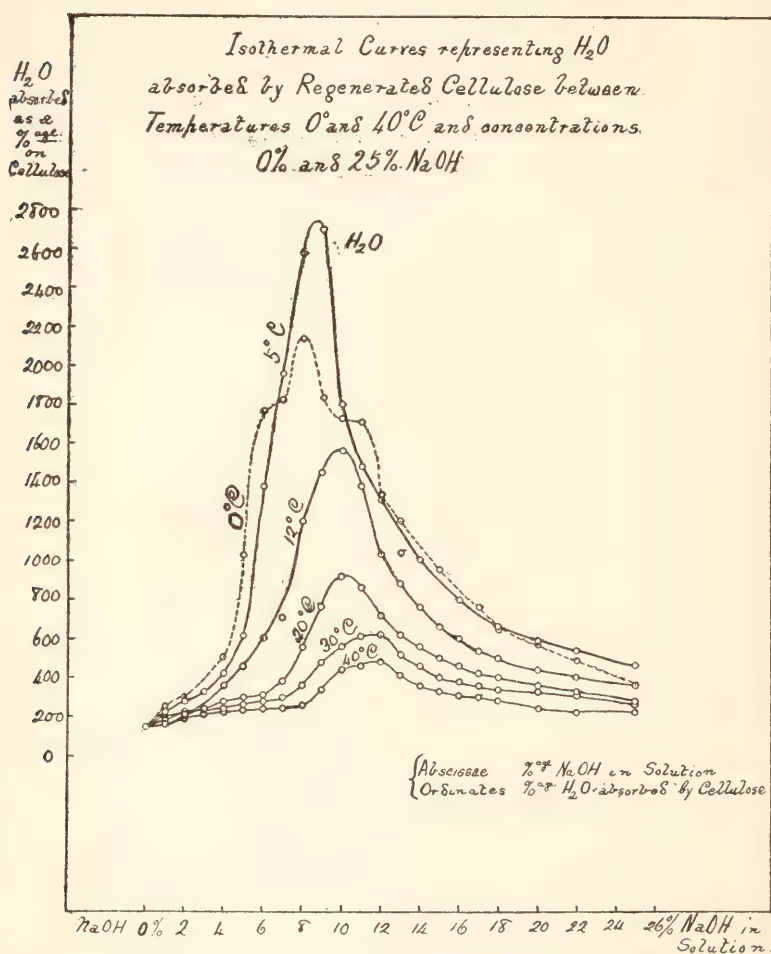


DIAGRAM 1

surface liquid. The total amount of alkali was determined in each by titration. The "hydration" figure was obtained by deducting the amount of NaOH found from the gain in weight. Both the hydration and NaOH absorption figures were calculated to a percentage on the original weight of cellulose. Before we settled upon a 30 minutes' immersion we made a number of trials, varying the period of immersion, and came to the conclusion that 30 minutes

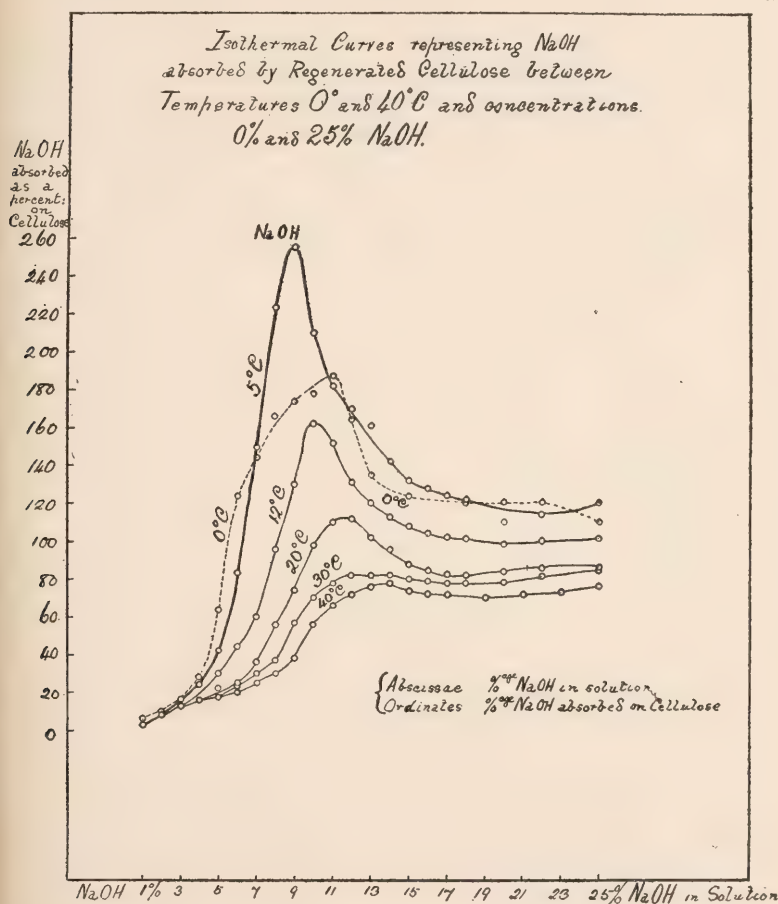


DIAGRAM 2

would best suit our purpose. It is our intention to make a further series of experiments for the purpose of determining the time required for equilibrium under different conditions.

The following figures show how far the results agree when repeated:

| NaOH in Bath | NaOH Absorption     |                     |
|--------------|---------------------|---------------------|
|              | 1st Series at 5° C. | 2nd Series at 5° C. |
| 4.0%         | 24                  | 23                  |
| 5.0%         | 42                  | 43                  |
| 6.0%         | 83                  | 83                  |

Had we taken precautions to read the temperatures more accurately the repetition figures would have been sufficiently close to be expressed to the first place of decimals. In the results recorded we have, however, omitted decimals and given the nearest round number. It must be understood that the results are in some measure determined by the conditions under which the thread has been manufactured. We therefore found it necessary to satisfy ourselves that the monofil used for the experiments was uniform in every particular.

TABLE A

| NaOH<br>in bath | HYDRATION<br>Cellulose = 100 |              |              |              |              | NaOH ABSORPTION<br>Cellulose = 100 |              |              |              |              |
|-----------------|------------------------------|--------------|--------------|--------------|--------------|------------------------------------|--------------|--------------|--------------|--------------|
|                 | at<br>5° C.                  | at<br>12° C. | at<br>20° C. | at<br>30° C. | at<br>40° C. | at<br>5° C.                        | at<br>12° C. | at<br>20° C. | at<br>30° C. | at<br>40° C. |
| 1.0%            | 217                          | 160          | 182          | 197          | 167          | 3                                  | 3            | 3            | 3            | 3            |
| 2.0%            | 279                          | 210          | 217          | 212          | 192          | 8                                  | 8            | 8            | 8            | 8            |
| 3.0%            | 324                          | 237          | 241          | 231          | 216          | 16                                 | 13           | 14           | 14           | 14           |
| 4.0%            | 426                          | 358          | 280          | 237          | 224          | 24                                 | 16           | 16           | 18           | 16           |
| 5.0%            | 615                          | 456          | 300          | 260          | 230          | 42                                 | 30           | 22           | 19           | 17           |
| 6.0%            | 1380                         | 600          | 310          | 278          | 238          | 83                                 | 44           | 25           | 23           | 20           |
| 7.0%            | 1960                         | 710          | 380          | 300          | 240          | 150                                | 60           | 36           | 30           | 25           |
| 8.0%            | 2576                         | 1200         | 562          | 360          | 261          | 224                                | 96           | 56           | 37           | 30           |
| 9.0%            | 2699                         | 1450         | 758          | 485          | 338          | 256                                | 130          | 74           | 57           | 38           |
| 10.0%           | 1800                         | 1558         | 920          | 558          | 440          | 210                                | 162          | 98           | 70           | 56           |
| 11.0%           | 1483                         | 1380         | 861          | 610          | 458          | 182                                | 152          | 110          | 78           | 66           |
| 12.0%           | 1310                         | 1030         | 719          | 620          | 480          | 170                                | 131          | 112          | 82           | 72           |
| 13.0%           | 1200                         | 885          | 620          | 519          | 412          | 161                                | 120          | 102          | 82           | 76           |
| 14.0%           | 1003                         | 760          | 558          | 460          | 360          | 142                                | 113          | 96           | 82           | 78           |
| 15.0%           | 798                          | 665          | 500          | 400          | 334          | 132                                | 108          | 88           | 80           | 74           |
| 16.0%           | 762                          | 600          | 458          | 385          | 310          | 128                                | 104          | 84           | 79           | 72           |
| 17.0%           | 715                          | 540          | 420          | 360          | 300          | 124                                | 102          | 82           | 78           | 71           |
| 18.0%           | 658                          | 500          | 400          | 340          | 280          | 122                                | 101          | 82           | 78           | 70           |
| 20.0%           | 590                          | 438          | 360          | 330          | 240          | 110                                | 98           | 84           | 78           | 72           |
| 22.0%           | 540                          | 400          | 325          | 310          | 220          | 114                                | 99           | 86           | 81           | 73           |
| 25.0%           | 461                          | 360          | 280          | 260          | 220          | 120                                | 101          | 86           | 84           | 76           |

Table A gives figures for hydration and NaOH absorption when the regenerated cellulose in question is immersed in so-

lutions of from 1% to 25% NaOH and at temperatures of 5°, 12°, 20°, 30°, and 40°C. As the results for 0°C. are of a somewhat different order from those of the foregoing we have given the figures for these separately in Table B.

TABLE B

| NaOH in Bath | Hydration at 0° C.<br>Cellulose=100 | NaOH absorption at<br>0° C. Cellulose=100 |
|--------------|-------------------------------------|---|
| 1.0%         | 254                                 | 6   |
| 2.0%         | 300                                 | 10  |
| 3.0%         | 331                                 | 14  |
| 4.0%         | 502                                 | 28  |
| 5.0%         | 1031                                | 64  |
| 6.0%         | 1766                                | 124                                       |
| 7.0%         | 1825                                | 144                                       |
| 8.0%         | 2135                                | 166                                       |
| 9.0%         | 1831                                | 174                                       |
| 10.0%        | 1727                                | 178                                       |
| 11.0%        | 1707                                | 188                                       |
| 12.0%        | 1336                                | 164                                       |
| 13.0%        | 1036                                | 134                                       |
| 15.0%        | 962                                 | 122                                       |
| 18.0%        | 650                                 | 120                                       |
| 20.0%        | 577                                 | 120                                       |
| 22.0%        | 490                                 | 120                                       |
| 25.0%        | 365                                 | 110                                       |

Diagram 1, plotted from Tables A and B, gives us the isothermal hydration curves and Diagram 2, similarly plotted, the isothermal soda (NaOH) absorption curves. To distinguish observations at 0°C. from the others they are plotted in broken line. It will be noticed that in the case of Diagram 1 the hydration for 0.0% NaOH is given, *i. e.*, gain in weight on immersion in water alone for 30 minutes. There is comparatively little difference for hydration in water alone for the different recorded temperatures.

Leaving out of consideration for the time being the observations at 0°C. and taking the case of Diagram 1, it will be noticed that for any given temperature (between 5°C. and 40°C.) a maximum hydration takes place, these maxima being greater the

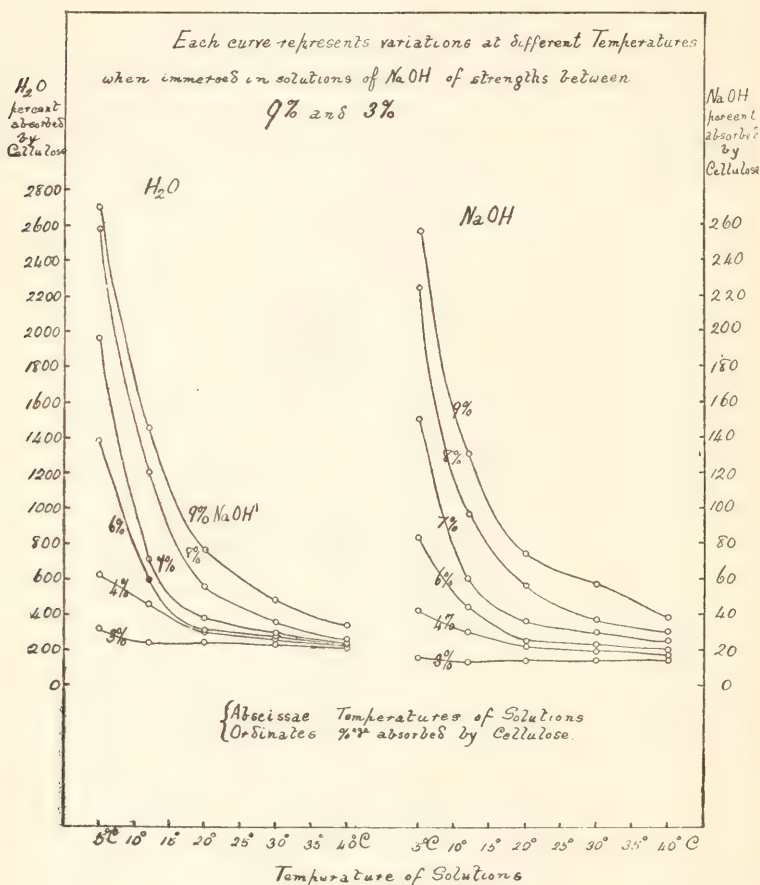


DIAGRAM 3

lower the temperature. At or near each maximum the difference per degree of temperature is greater, the lower the temperature. There is also a maximum at  $0^{\circ}C$ . but it falls below maximum for  $5^{\circ}C$ .

Although the maxima cannot be definitely placed without a greater number of observations in the neighbouring percentages, these maxima may be stated to occur as follows:



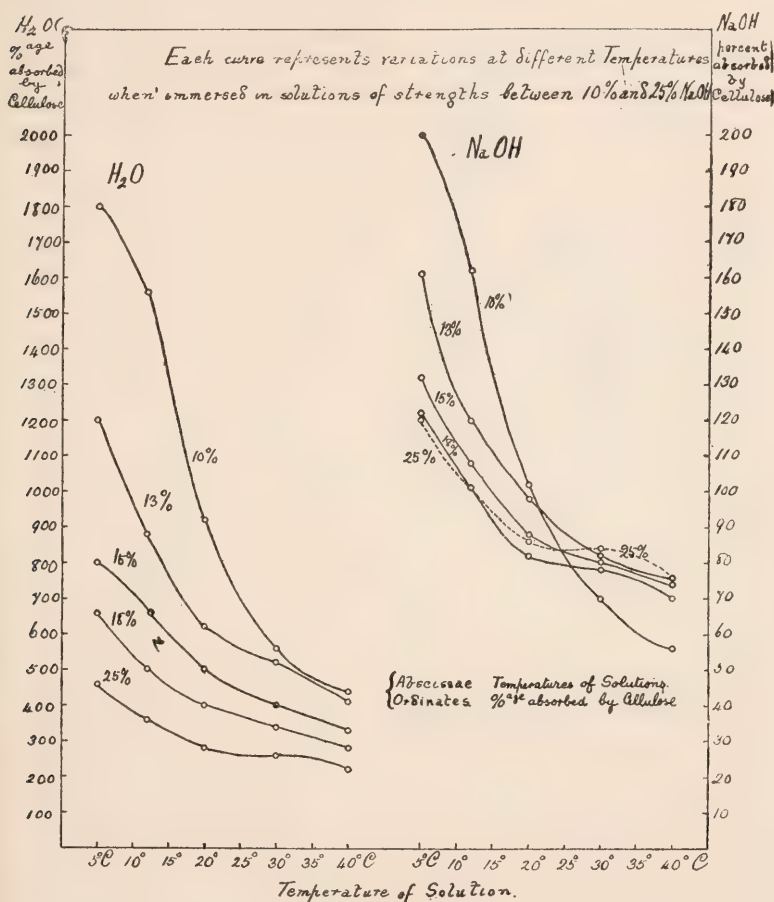


DIAGRAM 4

| °C.   |            | Solution   |      |
|-------|------------|------------|------|
| At 5  | in about   | 9%         | NaOH |
| At 12 | in about   | 10%        | NaOH |
| At 20 | in between | 10 and 11% | NaOH |
| At 30 | in between | 11 and 12% | NaOH |
| At 40 | in between | 11 and 12% | NaOH |

The same observations apply to the NaOH absorption. Here we have the following maxima:

|    | °C. |            | Solution   |      |
|----|-----|------------|------------|------|
| At | 5   | in about   | 9%         | NaOH |
| At | 12  | in about   | 10%        | NaOH |
| At | 20  | in between | 11 and 12% | NaOH |
| At | 30  | in between | 12 and 14% | NaOH |
| At | 40  | in about   | 14%        | NaOH |

The maxima for hydration and NaOH absorption therefore take place at greater concentrations as the temperature rises.

At 0°C. it will be observed that although we get a maximum hydration (at 8% NaOH) the curve is nothing like so regular. Also, the maximum soda absorption is at 11%. The behaviour at 0°C. is therefore of a different order from that of the other recorded temperature except that a maximum is reached.

Diagram 3 illustrates the effects of different temperatures upon hydration and NaOH absorption, in which each curve represents a different strength of mother liquor.

Diagram 4 is plotted in a similar manner to Diagram 3 but for percentages of mother liquor between 10% and 25% NaOH. Observe the difference in the character of the curves and their relationship to one another as concentration increases above 9% NaOH.

It will be observed that in 3% to 9% the hydration and NaOH absorption curves bear a fairly close resemblance to one another. If, in the process of swelling, the solution in which the cellulose is immersed were absorbed en masse and without change of composition, then the two sets of curves would be exactly similar to one another. The extent to which these two sets of curves differ from one another indicates the change of composition as the result of absorption (*i. e.* adsorption).

Table C is calculated for the purpose of showing how far the solution contained in the swollen mass differs in composition from that of the mother liquor. In the first column we have the strength of the mother liquor and under each of the temperature columns we have the actual strength (NaOH %) as contained in the swollen mass calculated to W/V basis in order to be comparable with column 1. After each figure is given the difference figure (+ or -) indicating the difference between the strength of the mother liquor and that absorbed by the swollen mass.

TABLE C

| Strength of Soda<br>solution used<br>NaOH % | Corresponding strength of Soda solution (NaOH%) as contained in swollen mass |      |      |      |       |      |       |      |       |      |       |      |  |  |
|---|--|------|------|------|-------|------|-------|------|-------|------|-------|------|--|--|
|   | Against each figure is placed the "difference"<br>figure (+ or -)            |      |      |      |       |      |       |      |       |      |       |      |  |  |
|   | 0°C.   |      | 5°C. |      | 12°C. |      | 20°C. |      | 30°C. |      | 40°C. |      |  |  |
| 1.0   | 2.2  | +1.2 | 1133 | +0.3 | 1188  | +0.8 | 1.6   | +0.6 | 1.5   | +0.5 | 1.7   | +0.7 |  |  |
| 2.0   | 3.0  | +1.0 | 2.8  | +0.8 | 3.6   | +1.6 | 3.4   | +1.4 | 3.5   | +1.5 | 3.8   | +1.8 |  |  |
| 3.0   | 3.9  | +0.9 | 4.5  | +1.5 | 5.9   | +2.9 | 5.2   | +2.2 | 5.4   | +2.4 | 5.7   | +2.7 |  |  |
| 4.0   | 5.0  | +1.0 | 5.2  | +1.2 | 4.0   | 0.0  | 5.1   | +1.1 | 6.6   | +2.6 | 6.2   | +2.2 |  |  |
| 5.0   | 5.5  | +0.5 | 6.0  | +1.0 | 5.8   | +0.8 | 6.4   | +1.4 | 6.4   | +1.4 | 6.4   | +1.4 |  |  |
| 6.0   | 6.2  | +0.2 | 5.4  | -0.6 | 6.4   | +0.4 | 7.4   | +1.4 | 7.1   | +1.1 | 7.3   | +1.3 |  |  |
| 7.0   | 6.8  | -0.2 | 6.6  | -0.4 | 7.2   | +0.2 | 8.6   | +1.6 | 9.5   | +2.5 | 8.6   | +1.6 |  |  |
| 8.0   | 6.7  | -1.3 | 7.4  | -0.6 | 7.0   | -1.0 | 8.3   | +0.3 | 9.9   | +1.9 | 9.3   | +1.3 |  |  |
| 9.0   | 8.0  | -1.0 | 7.8  | -1.2 | 7.6   | -1.4 | 8.2   | -0.8 | 9.5   | +0.5 | 9.0   | 0.0  |  |  |
| 10.0  | 8.5  | -1.5 | 9.4  | -0.6 | 8.6   | -1.4 | 8.7   | -1.3 | 9.7   | -0.3 | 10.1  | +0.1 |  |  |
| 11.0  | 9.0  | -2.0 | 9.9  | -1.1 | 9.0   | -2.0 | 10.1  | -0.9 | 10.1  | -0.9 | 11.2  | +0.2 |  |  |
| 12.0  | 9.4  | -2.6 | 10.2 | -1.8 | 10.0  | -2.0 | 11.9  | -0.1 | 10.4  | -1.6 | 11.5  | -0.5 |  |  |
| 13.0  | 10.7   | -2.3 | 10.6 | -2.4 | 10.7  | -2.3 | 12.4  | -0.6 | 12.0  | -1.0 | 13.5  | +0.5 |  |  |
| 14.0  | ...  | ...  | 11.0 | -3.0 | 11.5  | -2.5 | 12.9  | -1.1 | 13.2  | -0.8 | 15.2  | +1.2 |  |  |
| 15.0  | 10.1   | -4.9 | 12.5 | -2.5 | 12.3  | -2.7 | 13.0  | -2.0 | 14.3  | -0.7 | 15.4  | +0.4 |  |  |
| 16.0  | ...  | ...  | 12.7 | -3.3 | 12.9  | -3.1 | 13.5  | -2.5 | 14.6  | -1.4 | 15.9  | -0.1 |  |  |
| 17.0  | ...  | ...  | 13.0 | -4.0 | 13.7  | -3.3 | 14.1  | -2.9 | 15.1  | -1.9 | 16.1  | -0.9 |  |  |
| 18.0  | 13.5   | -4.5 | 13.6 | -4.4 | 14.4  | -3.6 | 14.6  | -3.4 | 15.8  | -2.2 | 16.7  | -1.3 |  |  |
| 20.0  | 14.8   | -5.2 | 13.6 | -6.4 | 15.5  | -4.5 | 16.0  | -4.0 | 16.1  | -3.9 | 19.3  | -0.7 |  |  |
| 22.0  | 16.6   | -5.4 | 15.0 | -7.0 | 16.7  | -5.3 | 17.5  | -4.5 | 17.3  | -4.7 | 20.4  | -1.6 |  |  |
| 25.0  | 19.4   | -5.6 | 17.3 | -7.7 | 18.4  | -6.6 | 19.7  | -5.3 | 20.1  | -4.9 | 20.7  | -4.3 |  |  |

It will be observed that at all recorded temperatures for low concentrations the absorbed solution is more concentrated than the unabsorbed or surrounding mother liquor, but at each temperature a point of concentration is reached at which the solution absorbed by the swollen hydrated cellulose synchronises in strength with that of the surrounding solution. This point, as will be observed, is somewhere about 6% for 0°C. and between 8 and 9% for 20°C., between 9 and 10% for 30°C.—in fact, there is a perfectly clear indication that the synchronising strengths advance in concentration as the temperature rises and that, within certain temperature limits, they bear some relation to, if they do not exactly correspond with, the strengths at which maxima occur such as are shown in Diagrams 1 and 2.

Table C also makes clear the point that, after reaching strengths at which the absorbed and external liquids synchronise in com-

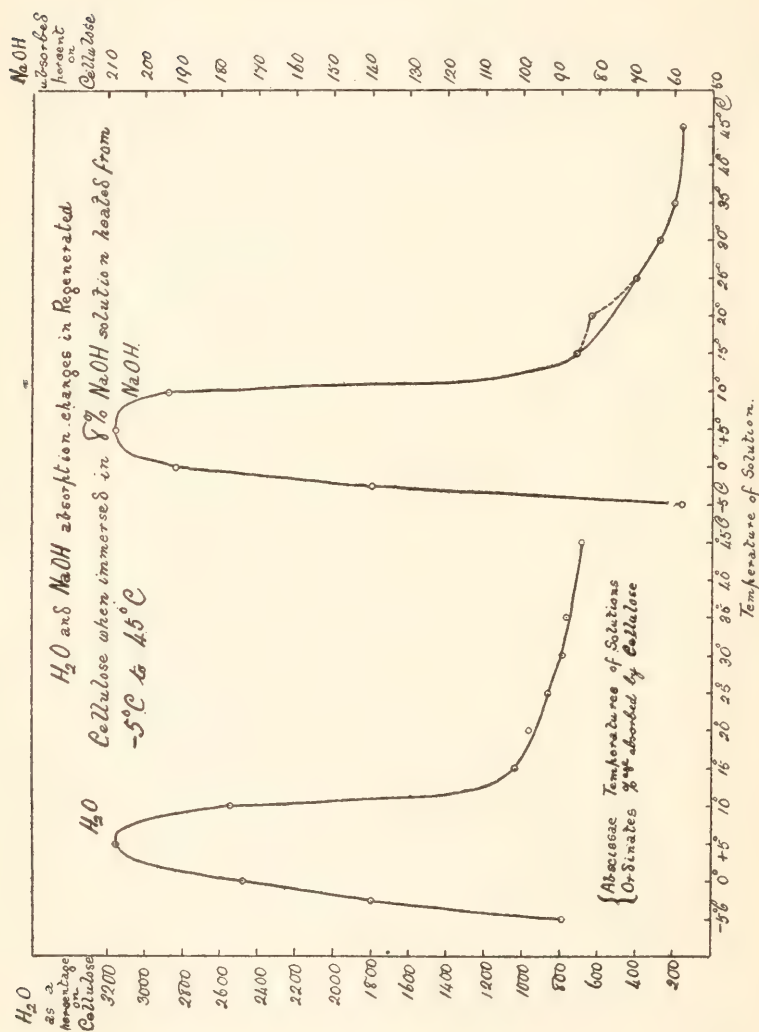
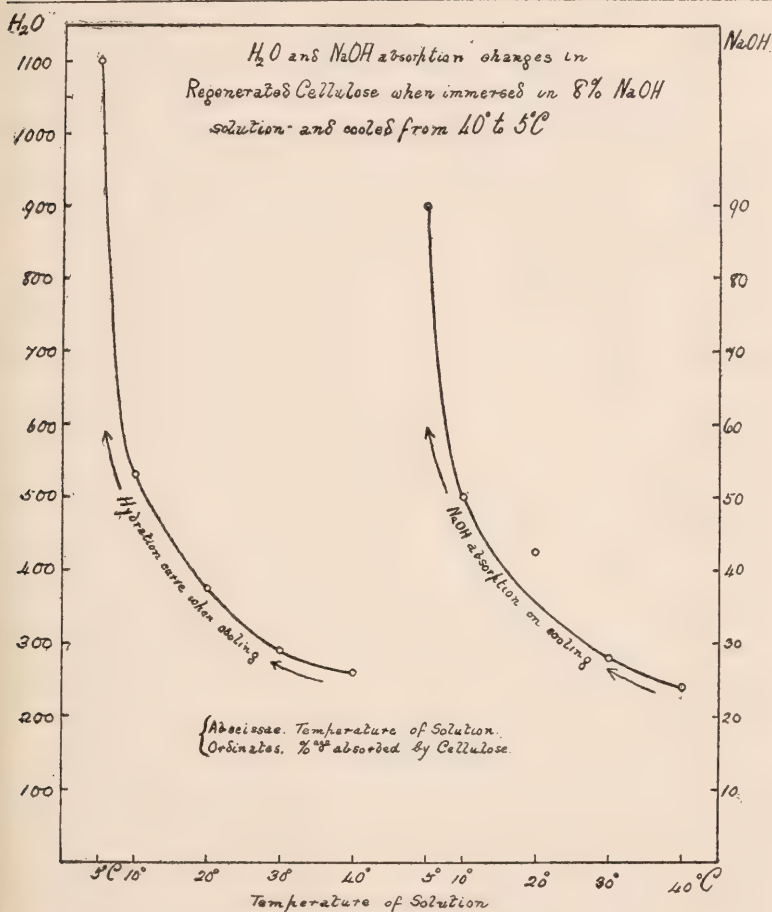


DIAGRAM 5



position as the concentration advances, the "difference" figure increases. Thus, at 0°C. and 9% NaOH the difference figure is in the neighbourhood of -1; at a concentration of 25% NaOH the difference figure is -5.6, and at 5°C. (for 25% NaOH) the difference figure is greater still (i.e. -7.7). It will be observed that the order in which the temperatures show the greatest "differences" at high concentrations (25%) corresponds with the order of maximum hydration and soda absorption as shown on Dia-



grams 1 and 2. The results rather indicate that the mother liquor concentration point of maximum hydration for any given temperature (Diagrams 1 and 2) corresponds somewhat with the point at which there is osmotic equilibrium (Table D), i.e., the point at which no difference exists between the composition of the absorbed liquid and the solution which surrounds it. If the two sets are not the same one set follows the other. Furthermore, that the temperature which gives in concentrated solution the greatest "difference" is also the temperature at which the greatest hydration is observable as a maximum and greatest differences in the hydration as the result of change of temperature.

In the results already recorded each figure was based on a test on an independent sample treated for 30 minutes. In order to see whether the same sample could be changed from one state of hydration to another, a sample similar to that used in the foregoing was placed in an 8% NaOH solution, the solution being slowly heated and the sample removed at intervals. The state of hydration is found to vary according to the temperature in the same manner as in the foregoing results (Diagram 3). One cannot, however, obtain exactly the same figures in this way without arresting the temperature at each point for say 30 minutes to establish equilibrium before removal of each sample.

For the purpose of investigating the influence of changing temperatures below 0°C., skeins were immersed in an 8% solution at -5°C. slowly heated to 45°C. and at intervals the hydration and soda absorption determined. In this case a number of the skeins were placed in the same mother liquor and taken out one at a time at convenient intervals as the temperature changed. 8% NaOH mother liquor was chosen for this and the foregoing as being the concentration which was most likely (judging from Diagrams 1 and 2) to show the greatest differences at different temperatures. It will be observed that in the neighbourhood of 5°C. we have a maximum and the curves on either side of the maximum appear to correspond very closely with one another until a temperature of about 14°C. is reached (see Diagram 5).

In Diagram 6 we have a similar set of experiments in which the cooling effect is observed between 40°C. and 5°C. The actual figures are without doubt influenced by the time of heating and

the time of cooling respectively. As the rate of change of temperature was fairly rapid, taking not more than one hour for each set of tests, equilibrium was not established at the time each sample was removed. Diagram 5 shows, however, that a maximum comes about at 5°C. for 8% NaOH, above which and below which for a few degrees there is rapid dehydration.

We have investigated the influence of common salt (NaCl) upon the hydration and NaOH absorption. If the regenerated cellulose is exposed under similar conditions to the foregoing (at 20°C., as recorded in Table A), to varying strengths of soda solution, which solution also contains 20% of NaCl, then the hydration varies only slightly compared with that containing no salt, increasing between 4% and 13% NaOH in mother liquor, above which latter strength it slightly diminishes. At its maximum hydration (at 5° C.) it is never more than about one-tenth of the hydration to be noticed in the absence of the NaCl.

The amount of NaCl absorbed by the regenerated cellulose has also been carefully determined. This remains fairly constant (at 5° C.) between 4% and 13% NaOH in mother liquor; at higher concentrations it diminishes.

The NaOH absorption, however, is a progressively increasing figure (at 5° C.) until one employs a mother liquor of 18% NaOH, after which it remains fairly constant up to a mother liquor of 25%. As the caustic soda is increased in strength from 15% to 25% (at 5° C.) in the presence of a constant proportion of NaCl (20%) the hydration diminishes, the NaCl absorption diminishes, whereas the NaOH absorption, if anything, increases. We have similarly investigated sodium sulphate. It is therefore evident that the addition of other soluble salts profoundly alters the hydration and the NaOH absorption, not only in degree but in kind. The influence of NaCl and other salts in this connection is being systematically studied and it is our intention that the same shall form a communication upon the subject when the work is further advanced.

In a case where the hydration figure was 1927 and the NaOH absorption 108 we added absolute alcohol and found the hydration diminished to 975 and the NaOH absorption to 36. Thinking that these results might in some way be connected with surface

tension, we tried the effect of adding 2% of soap in caustic soda solutions of 8%. We found no difference whatever in the figures for hydration and NaOH absorption as the result of the addition of the soap.

It is not our intention in this communication to arrive at an explanation of the results so far obtained, our object being merely to place them on record. We hope to offer an explanation at a later stage.

We were led to study these changes whilst investigating the manufacture of artificial silk and horsehair by what is known as the soda process of coagulation, which process has formed the subject of a large number of patents. The results herein recorded help to differentiate materially two classes of patents, one in which the thread is coagulated in soda alone and the other in soda plus salt. The results also serve to indicate the enormous importance of observing exact conditions in the manufacture of such products, particularly in regard to concentration and temperature of coagulating baths.

In conclusion we desire to thank Miss A. Borrowman and Mr. J. J. Watt for their assistance in the experimental work.

# THE PAPER MAKING QUALITIES OF THE HEDYCHIUM CORONARIUM

BY CLAYTON BEADLE AND HENRY P. STEVENS

*London, England*

This plant belongs to the order *Zingiberaceæ* and its order in the vegetable kingdom lies between the *Musaceæ* and *Cannaceæ*. It is described by Lindley as a plant with tuberous roots, herbaceous stems, clasping leaves and a terminal spicate inflorescence. It is distinguished by its handsome and fragrant flowers, especially the species *Hedychium Coronarium*.

The *Hedychium Coronarium*, like all members of the order, possesses an aromatic odor. The herb is tropical and found in Southern Asia as well as in South America. Several plants belonging to the same order are found in Ceylon and in the West Indies, also in parts of China. In some cleared lands where it has been planted it spreads like a carpet, by means of its rhizomes, to the exclusion of all other vegetable growth, and reaches a height of from one to two metres. Its relation to the *Musas* led us to think that perhaps it might be of service for textile purposes. We have this matter now under consideration, but the purpose of this communication is to describe only its paper-making qualities.

Photomicrograph<sup>1</sup> Fig. 1 shows a transverse section of two fibre-vascular bundles stained with Hæmatoxylin (Kleinenberg's formula), magnification 280 diameters. Photomicrograph Fig. 2 shows ultimate fibres, stained with chloride of zinc iodide magnification 125. Treating the transverse section with chloride of zinc iodide, the xylem portion of the fibro-vascular bundle is colored bright yellow, showing lignification, but when the fibre undergoes chemical treatment and is treated with the same reagent it is merely colored a pale violet. It will be noticed that, mixed with the fibres as prepared for paper making, there are a number of simple spiral vessels. We made a chemical analysis of the dried specimens as received with the following results:

<sup>1</sup>The photomicrographs are prepared by John Christie, F.R.M.S.



- A. Whole stem as gathered.  
 B. Whole stem after passing through crushing-rollers.

|                                 | A     | B     |
|---------------------------------|-------|-------|
| Moisture.....                   | 9.7%  | 11.2% |
| Ash .....                       | 4.5   | 4.8   |
| Cellulose.....                  | 43.0  | 48.0  |
| Extracted by chemical treatment | 42.8  | 36.0  |
|                                 | 100.0 | 100.0 |

|   |       |       |
|---|-------|-------|
| Cellulose air dry on air dry allow-<br>ing for losses ..... | 41.0% | 44.0% |
|---|-------|-------|

Raw material in the form of B is conveniently treated by boiling with 5% of soda at a pressure of three to five atmospheres. On washing this material, the yield of boiled product including all the fibrous constituents of the plant is 60%. The peculiar characteristics of the pulp are largely due to the presence of the oval cells of the pith, which is included in the above 60%. If these are removed by washing, the yield of fibre proper is 50% of unbleached material on the raw weight.

We discovered that the pith cells, which can be retained or not, according to requirements, possess very peculiar qualities. If taken alone, the unbleached cells when dried down go to a horny mass which can only be broken with very great difficulty with a hammer, and are softened only with difficulty when boiled in soda. If retained in the paper, they give it parchment-like properties to an extraordinary degree. They also render the paper ink bearing without the addition of any sizing material. Banana also can be made to possess ink-bearing qualities in the "waterleaf" form but it offers certain difficulties when run over the Fourdrinier paper machine which the *Hedygium* is free from. On the other hand, the paper made from *Hedygium* from which the cells are removed is of a soft nature and of medium strength but that in which the cells are retained, as will be seen, gives higher "breaking lengths" than any manila paper that we have so far had the opportunity of examining. The oval cells, therefore, "parchmentize," strengthen and size the sheet.





Y. S. F. V. BUNDLE HIDYCHIUM CORONARIUM. x 280.  
(SECTION STARRED HAMATOXYLIN.)



The pulp, after boiling in soda and beating, if examined under the microscope in the presence of chloriodide of zinc shows:

- (a) Oval cells stained blue.
- (b) Long wide fibres something like chemical wood, stained blue.
- (c) Numerous shorter and solid looking fibres, stained yellow.
- (d) Small epidermal cells attached to one another, stained yellow.

*Length of Fibres.* Table A gives the results of measurements under the microscope of

- 1. Hedychium fibres, unbleached, not beaten.
- 2. Hedychium bleached, not beaten.
- 3. Hedychium cells washed through 70-mesh wire, measured lengthwise.
- 4. Hedychium cells washed through 70-mesh wire, measured crosswise.
- 5. Best strong thick manila cable paper.
- 6. Ditto, thin.

TABLE A

| 1    |      | 2    |      | 3    |       | 4    |      | 5    |      | 6    |      |
|------|------|------|------|------|-------|------|------|------|------|------|------|
| mm.  | mm.  | mm.  | mm.  | mm.  | mm.   | mm.  | mm.  | mm.  | mm.  | mm.  | mm.  |
| 1.76 | 5.29 | 1.57 | .10  | .16  | .08   | .10  | 2.07 | 3.73 | 3.28 | 3.08 |      |
| 1.83 | 1.57 | 3.14 | .18  | .12  | .06   | .08  | 3.98 | 3.36 | 2.03 | 4.29 |      |
| 2.90 | 2.75 | 3.93 | .18  | .18  | .12   | .12  | 3.15 | 2.33 | 3.22 | 2.14 |      |
| 2.80 | 1.22 | .80  | .06  | .14  | .04   | .10  | 2.94 | 4.47 | 3.25 | 4.31 |      |
| 1.62 | 2.16 | 1.72 | .18  | .16  | .06   | .08  | 4.07 | 1.13 | 1.48 | 2.08 |      |
| 6.82 | 4.07 | 2.19 | .12  | .08  | .06   | .06  | 1.38 | 1.67 | 2.00 | 1.18 |      |
| 2.50 | 2.42 | 2.87 | .20  | .08  | .10   | .06  | 3.19 | 2.35 | 2.61 | 2.65 |      |
| 2.35 | 2.52 | 3.08 | .12  | .16  | .10   | .08  | 3.13 | 1.73 | 4.37 | 3.62 |      |
| 1.34 | 1.31 | 3.30 | .12  | .10  | .08   | .08  | 1.35 | 5.22 | 4.04 | 2.70 |      |
| 2.14 | 2.84 | 3.03 | .18  | .12  | .08   | .12  | 3.54 | 2.19 | 1.84 | 3.70 |      |
| Mean | 2.61 | 2.61 | 2.56 | .144 | .132  | .078 | .088 | 2.84 | 2.83 | 2.81 | 2.97 |
| Mean | 2.61 | 2.56 | .138 | .083 | 2.835 | 2.89 |      |      |      |      |      |

Mean of 3 and 4 = 0.110 mm.

It will be observed that the mean size of the cells, taking the mean of the two directions, is 0.11 mm., or less than 1/20 of the length of the fibres which measure 2.58. It can be understood, therefore, that such small particles as the oval cells will pass through a 70-mesh sieve of the washing drum, the holes of which would be about 0.2 mm., but the same sieve would of course retain the fibres proper. It will be observed also that the mean length of the fibres of the longest and strongest manila papers, which is about 2.85 mm., is only slightly in excess of that of the *Hedychium* fibre but, as will hereafter be seen, the *Hedychium*, on account of the peculiar nature of the fibres and the cells, is capable of producing a stronger and in many respects more serviceable paper. Moreover, the smallness of the *Hedychium* cells in comparison with the fibres enables the cells to fill the interstices between the fibres. Moreover, these cells, being of a flocculent, sticky and glutinous nature, act as a natural sizing material. We mechanically separated and weighed the cells and fibres with the following results:

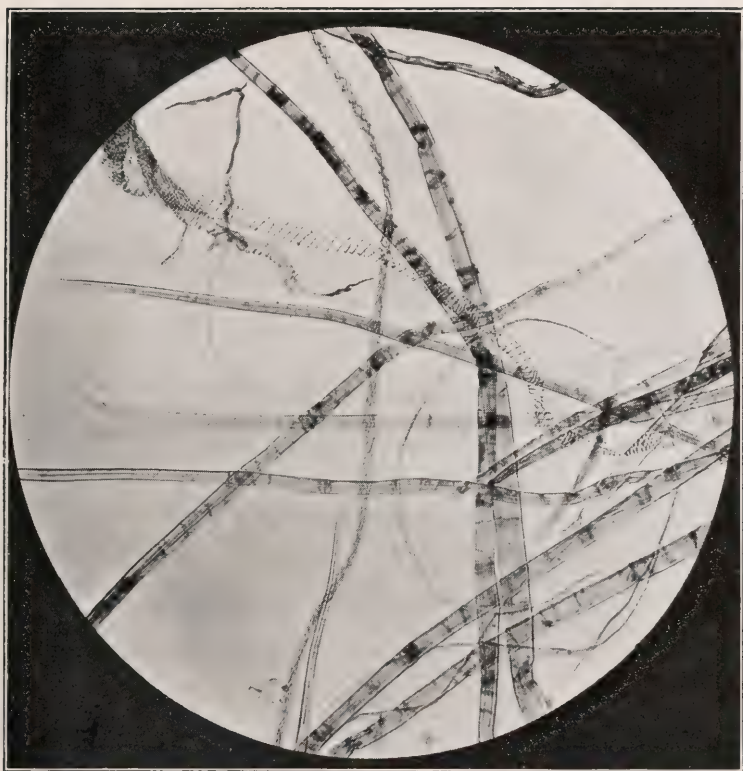
The actual amount of fibre proper and cells in *Hedychium* unbleached paper, the cells of which have been entirely retained, we find to be as follows:

|            |       |
|------------|-------|
| Cells..... | 17.3% |
| Fibre..... | 82.7% |

When the pulp is completely bleached so as to produce a white paper, the proportion by weight of cells and fibres in the finished paper is as follows:

|            |     |
|------------|-----|
| Cells..... | 14% |
| Fibre..... | 86% |

We have made several trials of this material on the paper machine. The beaten fibre, especially that containing the pith cells, when left in an unbleached condition, has an extremely greasy feel, enough to lead one to suppose that it would only part with its water with very great difficulty on the paper machine. Unlike most greasy feeling pulp, however, the water drains from the machine wire with great rapidity. We have seen the pulp on the wire of the paper machine on five or six occasions. In one case



ULTIMATE FIBRE HEDYCHUM CORONARIUM. x 125.  
(CHLOR. ZINC IODINE.)





TABLE B

|   | A    | B     | C    | D     | E     | F     | G     | H     | I     | J    | K     | L    | M     |
|---|------|-------|------|-------|-------|-------|-------|-------|-------|------|-------|------|-------|
| 1. Thickness in mm.   | .062 | .088  | .064 | .070  | .10   | .080  | .10   | ..... | .110  | .173 | .066  | .148 | .077  |
| 2. Substance. Demy lbs.<br><i>Strength in lbs. per inch width</i> | 8.9  | 14.1  | 9.2  | 10.0  | 19.9  | 13.3  | 20.2  | ..... | 20.9  | 31.6 | 27.1  | 26.3 | 11.4  |
| 3. Machine direction  | 8.6  | 26.9  | 13.5 | 18.8  | 37.0  | 21.5  | 44.6  | ..... | 41.3  | 42.7 | 24.3  | 73.8 | 12.88 |
| 4. Cross direction  | 6.0  | 13.3  | 6.7  | 9.5   | 27.3  | 18.5  | 29.4  | ..... | 17.2  | 26.2 | 14.7  | 25.0 | 12.00 |
| 5. Mean   | 7.3  | 20.1  | 10.1 | 14.2  | 32.2  | 20.0  | 37.0  | ..... | 29.2  | 34.4 | 19.5  | 49.4 | 12.44 |
| <i>Corrected to 0.1 mm. thick</i>                                 |      |       |      |       |       |       |       |       |       |      |       |      |       |
| 6. Machine direction  | 13.9 | 30.6  | 20.4 | 26.9  | 37.0  | 27.0  | 44.6  | ..... | 37.5  | 25.2 | 36.8  | 49.3 | 16.7  |
| 7. Cross direction  | 9.7  | 15.1  | 10.2 | 13.6  | 27.3  | 23.2  | 29.4  | ..... | 15.6  | 15.4 | 22.3  | 17.0 | 15.6  |
| 8. Mean   | 11.8 | 22.9  | 15.3 | 20.3  | 32.2  | 25.1  | 37.0  | ..... | 26.5  | 20.3 | 29.5  | 33.1 | 16.1  |
| 9. Breaking length in metres                                      | 6633 | 8018  | 8303 | 10083 | 8078  | 9381  | 9039  | 7950  | 6318  | 3204 | 5424  | 6286 | 7045  |
| <i>Stretch</i>  |      |       |      |       |       |       |       |       |       |      |       |      |       |
| 10. Machine direction   | 3.0% | 3.8%  | 4.1% | 3.8%  | 5.4%  | 4.6%  | 6.0%  | 2.8%  | 4.8%  | 4.2% | 4.6%  | 4.4% | 4.5%  |
| 11. Cross direction   | 7.0% | 10.2% | 8.8% | 8.2%  | 9.2%  | 9.5%  | 9.8%  | 7.8%  | 10.1% | 7.4% | 7.2%  | 13%  | 8.6%  |
| 12. Mean  | 5.0% | 7.0%  | 6.5% | 6.0%  | 7.3%  | 7.1%  | 7.9%  | 5.3%  | 7.5%  | 5.8% | 5.9%  | 8.7% | 6.6%  |
| <i>Final permanent elongation as measured after break</i>         |      |       |      |       |       |       |       |       |       |      |       |      |       |
| 13. Machine direction   | 2.6% | 3.4%  | 3.2% | 3.2%  | 2.6%  | 2.5%  | 3.4%  | ..... | 1.8%  | 2.0% | ..... | 1.8% | 1.8%  |
| 14. Cross direction   | 5.2% | 6.8%  | 7.0% | 6.6%  | 6.4%  | 6.5%  | 6.8%  | ..... | 3.0%  | 4.2% | ..... | 8.6% | 4.8%  |
| 15. Mean  | 3.9% | 5.1%  | 5.1% | 4.9%  | 4.5%  | 4.5%  | 5.1%  | ..... | 2.4%  | 3.1% | ..... | 5.2% | 3.3%  |
| <i>Bursting Strain (Eddy)</i>                                     |      |       |      |       |       |       |       |       |       |      |       |      |       |
| 16. Lbs. per sq. in.  | 14   | 24.2  | 11.3 | 13.7  | ..... | ..... | ..... | ..... | 32.0  | 44.4 | 28.6  | 63.6 | 21.1  |
| 17. Corrected to 0.1 mm.  | 17.2 | 20.7  | 14.8 | 17.8  | ..... | 4.50  | 55.0  | ..... | 29.1  | 26.0 | 43.4  | 43.0 | 27.4  |

TABLE B. — Continued.

|                           | A              | B              | C              | D     | E     | F     | G     | H     | I     | J     | K     | L     | M     |
|---------------------------|----------------|----------------|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| <i>Grease Proof Tests</i> |                |                |                |       |       |       |       |       |       |       |       |       |       |
| 18. Turpentine test       | { Not<br>proof | { Not<br>proof | { Not<br>proof | Proof | Proof | Proof | Proof | ..... | ..... | ..... | Proof | ..... | ..... |
| 19. Cold butter test      | { Not<br>proof | { Not<br>proof | { Not<br>proof | Proof | Proof | Proof | Proof | ..... | ..... | ..... | Proof | ..... | ..... |
| 20. Hot butter test       | { Not<br>proof | { Not<br>proof | { Not<br>proof | Proof | Proof | Proof | Proof | ..... | ..... | ..... | Proof | ..... | ..... |
| 21. Blister test          | { Not<br>proof | { Not<br>proof | { Not<br>proof | Proof | Proof | Proof | Proof | ..... | ..... | ..... | Proof | ..... | ..... |

## EXPLANATION OF HEADINGS TO TABLE B

- Column lbs.
- A. Hedychium  $\frac{1}{2}$  bleached 8 Large Post "Waterleaf."  
 B. Hedychium  $\frac{1}{2}$  bleached 12 Large Post "Waterleaf."  
 C. Hedychium  $\frac{1}{2}$  bleached 8 Large Post rosin sized.  
 D. Hedychium  $\frac{1}{2}$  bleached 9 Large Post rosin and gelatine sized.  
 E. Hedychium bleached white, beaten in Hollander.  
 F. Hedychium bleached white, beaten in Hollander.  
 G. The same as E and F but unbleached.  
 H. Pure manila paper as officially tested at the Berlin Testing House, 14th September, 1904.  
 I. Kraft B, supposed to be the best English make.  
 J. The best Kraft supplied by Messrs. James Spicer & Son, 16th November, 1911.  
 K. Vegetable parchment supplied by Messrs. James Spicer & Sons, retailed at 4d per lb.  
 L. English Matte pure manila imulating paper, thick.  
 M. English Matte pure manila imulating paper, thin.  
 The above papers A to D were boiled in 5% soda and washed in breaker so as to remove a great proportion of the cells.  
 E, F, G contain all the cells but no sizing material.

when making a parchment paper, we observed that the water left the wire quickly after the apron — in fact, in one-quarter of the space taken by a wood-pulp paper made on the same machine at the same speed. This argues in favor of the possibility of comparatively fast running on the paper machine, in spite of the greasy feel and the parchment-like qualities.

For the purpose of making a comparison of papers producible from the *H. Coronarium* with papers with which it is likely to come into competition, we carried out a number of tests as to strength, breaking strain, elongation, bursting strain and greaseproof qualities. These are contained in Table B.

We draw attention to this fibre as we believe it may become of great industrial importance to the paper trade. Where circumstances are congenial to its growth, the plant spreads to the exclusion of all other vegetable growth by means of its rhizomes, so that it can be harvested at least once a year, producing a heavy crop. It is an easy pulp to manipulate. It is capable of producing a paper of exceptional strength and can be worked either bleached or unbleached. The fact that the paper in its natural state, without the addition of any materials whatever, can be made to possess greaseproof and self-sizing qualities is a point of commercial importance.

Our thanks are due to Mr. John Christie for his kindness in preparing the photomicrographs.





## COMPOSITION OF COMMERCIAL GLUCOSE

BY ARTHUR P. BRYANT

*Clinton, Iowa*

It is well known that commercial glucose, or corn syrup, is a very complex material, containing a large number of intermediate products in the cleavage or hydrolysis of the starch molecule, ending with dextrose. In ordinary practise it is quite customary to determine the reducing value of the glucose and call it dextrose, while the remaining organic matter is called dextrin. There is present, however, a certain amount of maltose, and various methods have been proposed to determine the proportions of dextrose and maltose, which need not be referred to at this time further than to say that they usually ignore the possible presence of other reducing matter than dextrose and maltose.

When commercial glucose is fermented with yeast there is invariably found a residue which still shows a considerable reducing power towards Fehling solution. This may be due to the incomplete action of the yeast on the dextrose and maltose, or to the presence of some substance like the gallisin of Schmidt and Coblenz, or the isomaltose of Fischer, or it may be due to some of the less complex dextrins which, undoubtedly, have a reducing action on Fehling solution. It is unnecessary at this place to give a *résumé* of the literature on this subject, which is very considerable in amount. Moreover, it was not so much the object of these experiments to gain light on the exact nature of this residual product as to get some idea of the relative amounts of dextrose and maltose.

*Plan of the experiments.* Three series of experiments were carried on with commercial glucose from different sources. In two of these series 20 grams of glucose was made to 100 cc. and in the other series 10 grams to 100 cc. In the twenty per cent solutions brewers' yeast was used. This was washed free from all reducing matter, freed from excess moisture and used in the proportion of two grams per 100 cc. solution and the fermentation continued until there was no further lessening of the reducing

value, the temperature being maintained at 30–35° C. A little more yeast was then added and the test allowed to stand twenty-four hours longer, although in no instance was there evidence of further activity. The ten per cent solutions were fermented with two grams compressed yeast per 100 cc. until there was no further drop in the reducing value, and likewise let stand twenty-four hours more with fresh yeast.

The fermented solutions were then filtered and analyzed in the same way as the unfermented solutions. The determinations made were solids, reducing value, optical activity, ash, and in many cases nitrogen. Similar determinations were made upon a filtered solution of water and yeast with four per cent alcohol, which had been kept at the same temperature as the glucose solutions while the latter were fermenting. The results of the test on the blank showed that the yeast imparted no reducing material or optically active substance to the solution. The amount of solids in solution was extremely small, averaging not over one or two hundredths gram per 100 cc., most of which was apparently nitrogenous in character.

*Analytical methods.* Solids in the unfermented and fermented solutions were determined by drying on sand in vacuo at the temperature of boiling water. The reducing value was determined volumetrically by Fehling solution, the glucose solution being made to such strength that its reducing value was practically equivalent to that of a one per cent dextrose solution when this was practicable. However, the difference in reducing power for different concentrations appears to be very slight for dextrose and not very pronounced for maltose solutions, as will be seen from the table following. The specific rotary power was determined in a sugar scale polariscope. The sensitiveness of this instrument, unfortunately, was not sufficiently great to warrant fine distinctions being made in the results of different experiments. All determinations of reducing value and specific rotary power have been calculated to dry matter in the tables beyond.

*Relative reducing power of solutions of dextrose and maltose.* A chemically pure dextrose prepared by repeated crystallization of commercial dextrose from alcohol was dissolved in water in the proportion of 1.0 gram, .5 gram, .25 gram, and .1 gram, respec-

tively, per 100 cc., and the amount of dextrose in the solution determined volumetrically. Similar solutions were made with a so-called chemically pure maltose, with the exception that the highest concentration was 2 grams per 100 cc. and the lowest .25 grams per 100 cc. The relative reducing power of this sugar as well as its specific rotary power showed that it was not a strictly pure maltose, but no attempt was made to purify it.

A comparison of the amounts of reducing sugar in the various solutions actually present as compared with amounts found is shown below:

| Sugar in 100 cc.  |                  | Sugar Found<br>Dextrose Equivalent<br>Grams | Sugar Found<br>As Maltose<br>(Factor .62)<br>Grams |
|-------------------|------------------|---|--|
| Dextrose<br>Grams | Maltose<br>Grams |   |  |
| 1.000             | .....            | 1.000                                       | .....  |
| 1.000             | .....            | 1.000                                       | .....  |
| .500              | .....            | .500  | .....  |
| .500              | .....            | .500  | .....  |
| .500              | .....            | .496  | .....  |
| .250              | .....            | .248  | .....  |
| .250              | .....            | .248  | .....  |
| .100              | .....            | .100  | .....  |
| .100              | .....            | .100  | .....  |
| .....             | 2.000            | 1.116                                       | 1.800  |
| .....             | 2.000            | 1.116                                       | 1.800  |
| .....             | 1.000            | .571  | .921   |
| .....             | 1.000            | .571  | .921   |
| .....             | .500             | .272  | .439   |
| .....             | .500             | .270  | .435   |
| .....             | .250             | .136  | .219   |
| .....             | .250             | .136  | .219   |

*Completeness of fermentation.* In order to compare the completeness of fermentation under the conditions of these experiments ten per cent solution of sucrose, dextrose and maltose were made and treated in exactly the same way and at the same time as the experiments with glucose. The dextrose contained a little moisture which was not removed for these tests. Results are as follows:

| 10% Solution                         | Sucrose<br>% | Dextrose<br>% | Maltose<br>% |
|--------------------------------------|--------------|---------------|--------------|
| Solids, % by volume,                 | 10.00        | 9.50          | 9.96         |
| Solids after fermentation,           | .07          | .04           | .04          |
| Residual reducing value as dextrose, | .01          | .02           | .03          |
| Nitrogen,                            | .015         | ....          | ....         |

A blank solution run at the same time showed .01% solids. The .03% reducing value of maltose at the end of the fermentation would be equivalent to .05% actual maltose still unfermented.

*Dialysis of sugar solutions.* Experiments were run in which glucose and the unfermented residue were submitted to dialysis in running water in vegetable parchment tubes. In order to determine the length of time necessary to dialyze dextrose and maltose solutions, ten per cent concentrations were made and dialyzed until the solution in the parchment showed no further reducing value. At the same time ten per cent solutions of two commercial dextrans were submitted to dialysis. The results were as follows:

|   | Dextrose<br>Solution<br>Grams | Maltose<br>Solution<br>Grams |
|---|-------------------------------|------------------------------|
| Solids in 100 cc.,                            | 9.500                         | 9.850                        |
| Solids remaining in 12 hours,                 | .450                          | 1.650                        |
| 24 hours,                                     | .036                          | .770                         |
| 36 hours,                                     | .011                          | .390                         |
| 48 hours,                                     | .000                          | .210                         |
| 60 hours,                                     | .....                         | .028                         |
| 72 hours,                                     | .....                         | .000                         |
|   | "C Dextrin"                   | "British Gum"                |
| Solids in 100 cc.,                            | 9.65                          | 9.32                         |
| Solids remaining in 24 hours,                 | 8.17                          | 8.55                         |
| Solids remaining in 48 hours,                 | 7.55                          | 7.90                         |
| Per cent dialyzed,                            | 21.8                          | 15.2                         |
| Dextrose equivalent at start,                 | .980                          | .240                         |
| Dextrose equivalent at end,                   | .507                          | .186                         |
| Per cent dialyzed,                            | 48.2                          | 22.5                         |
| Dextrose equivalent material dialyzed,        | 22.5%                         | 3.8%                         |
| Dextrose equivalent material not<br>dialyzed, | 6.8%                          | 2.4%                         |



From the above results it will be seen that the dialysis of dextrose and maltose should be practically complete in forty-eight hours and that there is evidently a considerable dialysis of either dextrose, maltose, or reducing dextrins in the case of commercial dextrins.

*Description of samples.* Samples A to I were secured from various parts of the country and represent the product of various companies manufacturing glucose. All but the last sample, I, were made from the starch of maize, while sample I was manufactured from potato starch and imported. Samples J to M are another representative line of glucose samples as put out by four different concerns. Samples N, O and P represent separate steps in the hydrolysis of starch in the manufacture of glucose. Sample N was taken from the "converter" when the hydrolysis had been going on about one-third the full required time. Sample O represents the same "conversion" after about two-thirds the time had elapsed, while sample P was taken from the finished "boil" after hydrolysis had been checked by removal of pressure and the neutralization of acidity.

Samples Q to T were treated with compressed yeast, the glucose being identical with that used in J to M respectively. It will be observed that fermentation, although complete for that kind of yeast, was decidedly less than with brewers' yeast.

*Results of the experiments.* The following table gives the analytical results obtained in these tests. The solids were for the most part determined by drying on sand as already stated, and in nearly all cases results thus determined were corroborated by determination of the refractive index and the per cent Brix. The "dextrose equivalent" is the reducing value calculated as dextrose. Percentages are all by volume, or grams per 100 cc.

In the following table is shown the computed dextrose value (K) of the dry material before and after fermentation, also the specific rotary power ( $S_d$ ) of the dry material before and after. The last four columns of the table show the computed composition of the glucose.

The determination of the unfermented residue in glucose suffices for the estimation of the proportions of dextrose and maltose upon the supposition that no other reducing material is fermented.



## RESULTS OF ANALYSIS OF GLUCOSE SOLUTION BEFORE AND AFTER FERMENTATION AND DIALYSIS

| MATERIAL      | IN ORIGINAL SOLUTION |                             |   |          | IN FERMENTED SOLUTION |                      |                             |   | AFTER DIALYSIS<br>UNFERMENTED SOLUTION |      |                      |                             |   |
|---------------|----------------------|-----------------------------|---|----------|-----------------------|----------------------|-----------------------------|---|--|------|----------------------|-----------------------------|---|
|               | Solids in<br>100 cc. | Dextrose<br>Equiva-<br>lent | Reading<br>on Sugar<br>Scale <sup>1</sup> | Nitrogen | Ash                   | Solids in<br>100 cc. | Dextrose<br>Equiva-<br>lent | Reading<br>on Sugar<br>Scale <sup>2</sup> | Nitrogen                               | Ash  | Solids in<br>100 cc. | Dextrose<br>Equiva-<br>lent | Reading<br>on Sugar<br>Scale <sup>1</sup> |
|               | grams                | %                           | °   | %        | %                     | grams                | %                           | °   | %                                      | %    | grams                | %                           | °   |
| Glucose A     | 16.63                | 7.94                        | 64.5                                      | .003     | .06                   | 7.86                 | 1.49                        | 68  | ....                                   | .06  | ....                 | ....                        | ....                                      |
|               | 16.54                | 8.01                        | 64.0                                      | .003     | .06                   | 8.00                 | 1.51                        | 70  | ....                                   | .06  | ....                 | ....                        | ....                                      |
|               | 16.60                | 8.09                        | 63.5                                      | .003     | .06                   | 8.05                 | 1.52                        | 72  | ....                                   | .06  | ....                 | ....                        | ....                                      |
|               | 16.30                | 6.84                        | 65.0                                      | .002     | .10                   | 9.05                 | 1.51                        | 82.5                                      | ....                                   | .10  | ....                 | ....                        | ....                                      |
|               | 16.34                | 7.31                        | 65.0                                      | .002     | .12                   | 8.50                 | 1.50                        | 80  | ....                                   | .12  | ....                 | ....                        | ....                                      |
|               | 16.04                | 7.00                        | 64.5                                      | .002     | .07                   | 8.50                 | 1.49                        | 77.5                                      | ....                                   | .07  | ....                 | ....                        | ....                                      |
|               | 16.30                | 7.25                        | 64.5                                      | .005     | .08                   | 8.75                 | 1.52                        | 81  | ....                                   | .08  | ....                 | ....                        | ....                                      |
|               | 16.48                | 7.25                        | 65.0                                      | .005     | .06                   | 8.87                 | 1.54                        | 82.5                                      | ....                                   | .06  | ....                 | ....                        | ....                                      |
|               | 17.24                | 8.70                        | 64.5                                      | .001     | .07                   | 7.80                 | 1.56                        | 68.5                                      | ....                                   | .07  | ....                 | ....                        | ....                                      |
|               | 16.88                | 7.96                        | 64.5                                      | .002     | .10                   | 9.17                 | 1.80                        | 85.0                                      | .015                                   | .10  | 5.15                 | 1.20                        | 46.2                                      |
| Glucose J     | 16.71                | 6.72                        | 69.0                                      | trace    | .10                   | 10.03                | 1.81                        | 97.5                                      | .008                                   | .11  | 6.30                 | 1.44                        | 55.0                                      |
|               | 17.05                | 7.40                        | 68.5                                      | .003     | .10                   | 9.50                 | 1.76                        | 90.5                                      | .011                                   | .10  | 5.25                 | 1.36                        | 45.7                                      |
|               | 17.05                | 8.50                        | 65.2                                      | .003     | .08                   | 8.44                 | 1.75                        | 77.5                                      | .009                                   | .10  | 4.84                 | 1.14                        | 43.5                                      |
|               | 20.61                | 6.01                        | 92.6                                      | .005     | .10                   | 14.26                | 2.08                        | 73.0 <sup>1</sup>                         | .015                                   | .11  | 8.36                 | 1.45                        | 82.3                                      |
|               | 20.32                | 7.40                        | 86.0                                      | .005     | .10                   | 13.06                | 2.23                        | 63.5 <sup>1</sup>                         | .020                                   | .10  | 6.46                 | 1.20                        | 60.0                                      |
|               | 20.55                | 9.40                        | 77.6                                      | .005     | .10                   | 11.20                | 2.19                        | 104.0                                     | .020                                   | .11  | 4.68                 | 1.15                        | 43.0                                      |
|               | 10.00                | ....                        | ....                                      | ....     | ....                  | .04                  | .01                         | ....                                      | .006                                   | .... | .10                  | ....                        | ....                                      |
|               | 9.50                 | 9.50                        | ....                                      | ....     | ....                  | .04                  | .02                         | ....                                      | .006                                   | .... | ....                 | ....                        | ....                                      |
|               | 9.96                 | 5.68                        | ....                                      | ....     | ....                  | .04                  | .02                         | ....                                      | .006                                   | .... | .21                  | .12                         | ....                                      |
|               | 9.65                 | .98                         | ....                                      | ....     | ....                  | ....                 | ....                        | ....                                      | ....                                   | .... | 7.55                 | .51                         | ....                                      |
| Glucose Q (J) | 9.32                 | .24                         | ....                                      | ....     | ....                  | ....                 | ....                        | ....                                      | ....                                   | .... | 7.90                 | .19                         | ....                                      |
|               | 8.32                 | 3.92                        | ....                                      | ....     | .05                   | 5.49                 | 1.42                        | ....                                      | ....                                   | .... | ....                 | ....                        | ....                                      |
|               | 8.30                 | 3.33                        | ....                                      | ....     | .05                   | 5.78                 | 1.30                        | ....                                      | ....                                   | .... | ....                 | ....                        | ....                                      |
|               | 8.32                 | 3.60                        | ....                                      | ....     | .05                   | 5.44                 | 1.23                        | ....                                      | ....                                   | .... | ....                 | ....                        | ....                                      |
|               | 8.33                 | 4.14                        | ....                                      | ....     | .04                   | 5.24                 | 1.45                        | ....                                      | ....                                   | .... | ....                 | ....                        | ....                                      |

Thus: Let D equal dextrose, M equal maltose, K equal reducing value as dextrose, F equal amount fermented and .62 the relative reducing value of maltose as compared with dextrose.

$$\text{Then } D + .62 M = K$$

$$D + M = F$$

$$\text{Subtracting } .38 M = F - K$$

The composition of the unfermentable material cannot be determined as definitely as that of the fermentable. If, as is altogether probable, the reducing value of the unfermentable residue is due to a reducing dextrin, it would certainly be difficult to determine in actual composition. On the other hand, if it is due to isomaltose or gallisin, we are confronted by the fact that there is a very large amount of this material, although hydrolysis has not been carried very far. Moreover, an attempt to obtain a characteristic osazone of this unfermentable residue failed, no osazone separating in either the hot or cold solution. With commercial glucose the osazone of both dextrose and maltose was separated without difficulty. In the unfermentable residue of grape sugar, however, Bryant and Miner found a material giving an osazone which strongly suggested the presence of some such material as gallisin or isomaltose.

*Discussion of results.* Among the interesting points brought out by these tests is the fairly approximate agreement between the dextrose value and the total fermentable sugars, the average of tests A to P showing 44.1% for the dextrose equivalent and 45.9% for the fermentable matter. In other words, for all practical purposes the determination of the reducing value of the glucose as dextrose gives a fairly close measure of the total fermentable matter.

There is much less variation in the proportion of maltose than of dextrose and the lower the total amount of reducing sugars the less the dextrose until in the early stages of hydrolysis (see Experiment N) there is no dextrose at all. Maltose appears to be formed first and then inverted with formation of dextrose.

There is a marked uniformity in the reducing value of the unfermentable residue which strongly suggests that there is an ap-

## COMPOSITION OF DRY SUBSTANCE OF COMMERCIAL GLUCOSE

| MATERIAL         | ORIGINAL MATERIAL DRY SUBSTANCE |                                      | UNFERMENTED RESIDUE DRY SUBSTANCE |   |                                      |                                      | COMPUTED COMPOSITION |         |          |       |
|------------------|---------------------------------|--------------------------------------|-----------------------------------|---|--------------------------------------|--------------------------------------|----------------------|---------|----------|-------|
|                  | Dextrose Value K                | Specific Rotary Power S <sub>d</sub> | Dextrose Value K <sub>i</sub>     | Dextrose Value in Terms Original Material K | Specific Rotary Power S <sub>d</sub> | Proportion Original Solids Fermented | Dextrose             | Maltose | Dextrins | Ash   |
| Glucose A        | 47.7                            | °                                    | 18.9                              | 8.9   | 152                                  | 52.7                                 | 16.1                 | 36.6    | 47.0     | 0.3   |
| B                | 48.4                            | 134                                  | 18.9                              | 9.2   | 153                                  | 51.6                                 | 19.0                 | 32.6    | 48.1     | 0.3   |
| C                | 48.7                            | 134                                  | 18.9                              | 9.2   | 153                                  | 51.5                                 | 19.9                 | 31.6    | 48.2     | 0.3   |
| D                | 42.3                            | 139                                  | 16.7                              | 9.3   | 162                                  | 44.5                                 | 14.2                 | 30.3    | 54.9     | 0.6   |
| E                | 44.7                            | 139                                  | 17.7                              | 9.2   | 154                                  | 48.0                                 | 12.5                 | 35.5    | 51.3     | 0.7   |
| F                | 43.6                            | 141                                  | 17.5                              | 9.3   | 160                                  | 47.0                                 | 14.6                 | 32.4    | 52.6     | 0.4   |
| G                | 44.4                            | 140                                  | 17.4                              | 9.3   | 164                                  | 46.3                                 | 16.8                 | 29.5    | 53.2     | 0.5   |
| H                | 44.0                            | 139                                  | 17.3                              | 9.3   | 164                                  | 46.2                                 | 15.9                 | 30.3    | 53.4     | 0.4   |
| I                | 50.5                            | 132                                  | 19.4                              | 9.0   | 155                                  | 54.8                                 | 19.8                 | 35.0    | 44.8     | 0.4   |
| Glucose J        | 47.2                            | 132                                  | 19.6                              | 10.7  | 160                                  | 45.7                                 | 21.5                 | 24.2    | 53.8     | 0.5   |
| K                | 40.2                            | 143                                  | 18.0                              | 10.8  | 168                                  | 40.0                                 | 12.1                 | 27.9    | 59.5     | 0.5   |
| L                | 43.4                            | 139                                  | 18.5                              | 10.3  | 164                                  | 44.3                                 | 14.8                 | 29.5    | 55.3     | 0.4   |
| M                | 49.8                            | 132                                  | 20.7                              | 10.3  | 159                                  | 50.5                                 | 21.6                 | 28.9    | 49.1     | 0.4   |
| N                | 29.2                            | 155                                  | 14.6                              | 10.1  | 177                                  | 30.8                                 | 0.0                  | 30.8    | 68.8     | 0.4   |
| O                | 36.4                            | 146                                  | 17.1                              | 11.0  | 168                                  | 35.7                                 | 8.6                  | 27.1    | 63.9     | 0.4   |
| P                | 45.7                            | 130                                  | 19.6                              | 10.6  | 160                                  | 45.5                                 | 18.1                 | 27.4    | 54.1     | 0.4   |
| Average 16 tests | 44.1                            |                                      |                                   |   |                                      | 45.9                                 |                      |         |          |       |
| Sucrose          | 0.0                             | 67                                   | .....                             | .....                                       | .....                                | 99.9                                 | .....                | .....   | .....    | ..... |
| Dextrose         | 100.0                           | 53                                   | .....                             | .....                                       | .....                                | 99.8                                 | .....                | .....   | .....    | ..... |
| Maltose          | 57.0                            | 130                                  | .....                             | .....                                       | .....                                | 99.7                                 | .....                | .....   | .....    | ..... |
| Glucose Q (J)    | 47.1                            | ...                                  | 25.9                              | 17.1  | ...                                  | 34.0                                 | 12.7                 | 21.3    | 65.5     | 0.5   |
| R (K)            | 40.1                            | ...                                  | 22.5                              | 15.7  | ...                                  | 30.4                                 | 9.6                  | 20.8    | 69.1     | 0.5   |
| S (L)            | 43.3                            | ...                                  | 22.4                              | 14.7  | ...                                  | 34.6                                 | 2.5                  | 32.1    | 65.0     | 0.4   |
| T (M)            | 49.7                            | ...                                  | 27.7                              | 17.4  | ...                                  | 37.1                                 | 12.4                 | 24.7    | 62.5     | 0.4   |

proximately constant proportion of the dextrins having an action on Fehling solution, maltose being formed by hydrolysis of these simpler dextrins at approximately the same rate that the more complex dextrins are broken down into the simpler forms.

The longer the action of the acid on the starch and its cleavage products, the more maltose is inverted. A high degree of conversion is, therefore, indicative of a relatively large dextrose content, and a low degree of conversion of a relatively small dextrose content, the maltose remaining practically the same in all cases.<sup>1</sup>

Experiments with fermentation of dextrose and maltose indicate that the action of the yeast is practically complete. Failure to obtain an osazone from the unfermented residue bears out this supposition.

The four experiments with ordinary compressed yeast give results strongly indicative of incomplete fermentation, although no further action took place on a longer treatment with fresh yeast. No comparisons on fermentation of pure dextrose and maltose by means of compressed yeast were made. The results of these experiments, Q to T, are, therefore, not worthy of comparison with those of the other experiments.

Experiments on the dialysis of glucose show that the most of the reducing sugars and also much of the dextrin passed through the membrane. Treatment of the undialyzed residue with phenylhydrazine gives dextrosazone and maltosazone and shows that at the end of two days there still remained some of these sugars which had not dialyzed. Dialysis of the unfermentable residues showed a reduction in the total solids but no great change in the relative reducing values. Experiments on the dialysis of dextrose and maltose show that in two days all of the former and practically all of the latter sugar had been removed from the solution.

#### SUMMARY

The determination of the dextrose equivalent of the glucose gives a close measure of the total amount fermentable, but the

<sup>1</sup>Experiments by the writer and C. S. Miner indicate, however, that in grape sugar, where hydrolysis has been carried on to a much greater degree than in glucose, all the maltose has been changed to dextrose.

larger part of the fermentable sugar is maltose, which is fairly constant in amount, averaging roughly 30% of the dry substance.

Hydrolysis of starch under conditions existing in the manufacture of commercial glucose appears to yield a nearly constant amount of reducing dextrins and maltose, while the dextrose varies widely in amount according to the "degree of conversion."



## A STUDY OF THE UNFERMENTABLE RESIDUE IN HYDROLITIC PRODUCTS OF STARCH

BY A. P. BRYANT AND C. S. MINER

*Clinton, Iowa, and Chicago, Illinois*

In the hydrolysis of starch it has long been recognized that there is frequently found an unfermentable but reducing residue, which differs from pure dextrose or maltose or other sugar on the one hand and from the dextrans on the other. The first work of any especial importance was done by Schmitt and Coblenz (Ber. 17-1000-and 2464), who obtained from this unfermentable residue a substance which they called gallisin. They determined its properties but by methods which were open to criticism. Scheibler and Mittelmeier (Ber. 23-3075), a few years later went over the same ground with considerable care. They obtained a fairly pure material and determined its properties. In the same year Emil Fischer (Ber. 23-3687) published an account of an osazone which he had prepared from grape sugar. This showed about the same properties as the osazone from the gallisin of Scheibler & Mittelmeier. Fischer named his material isomaltose. Subsequent to this considerable work was done, mainly by Lintner and Dull (Ber. 26-2533-28-1523), for the purpose of proving that isomaltose occurred in the products of diastatic fermentation, but this theory was vigorously combatted and finally discredited. The work done at this time by Brown and Morris (Ch. N. 72-45), by Ling and Baker (Ch. N. 71-71), and by Ost (Ch. Z.-19-1504), seemed to prove conclusively that the isomaltose of Lintner and Dull was a mixture of maltose with dextrans. Ost went further than the others and attacked Fischer's isomaltose, but Fischer's vigorous defense as well as the later re-searches of Ost, Ch. Z. 20-762, seemed to prove the existence of isomaltose. The unsatisfactory state of our information upon this subject is well stated by Lippman (Chemie der Zuckerarten-Vol. II, page 1504) in his excellent bibliography and brief synopsis of the work done along this line, who says that while all investigations known to

him are referred to all, with the exception of Fischer's work on isomaltose, are to be considered as of more or less uncertain value.

For the purpose of studying the unfermentable residue in different hydrolytic products manufactured from starch, the following experiments were made. These are to be regarded as incomplete and the results are published at this time without the attempt to claim or disclaim definitely that gallisin or isomaltose is present in these products, but simply as additional data regarding the composition of starch hydrolytic products.

The aim has been to remove all of the sugars by means of yeast fermentation and then examine the unfermentable residue. Various proportions of sugar, yeast and water were used but the best results were obtained by using a 20% sugar solution, adding 5 grams yeast to 100 cc sugar and allowing fermentation to continue for ten to fourteen days. As a check on complete fermentation under these conditions, a like amount of yeast was added to the unfermented residue after the alcohol had been removed and the material concentrated to about its original density, but there was no evidence of further action.

The unfermented residue was examined both before the removal of the alcohol, and after the alcohol had been driven off and the solution concentrated. The reducing value "K", in terms of dextrose was determined and the specific rotary power for the sodium ray. The value "K" was determined volumetrically by means of a Fehling solution standardized by use of pure dextrose before each experiment. The rotation was observed in a Schmidt-Haensch circular scale instrument after cleaning with alumina cream and without addition of lead acetate. Sodium light was employed. Several kinds of commercial and brewers' yeasts were tried, but the best results were obtained by using a special yeast, which was found to contain no soluble reducing matter or optically active bodies. Fermentation was allowed to proceed at room temperature.

Experiments were made with the following materials:

Expt. 1. Glucose or starch syrup, Be. 43° at 100F, water 17.2%, 10 grams glucose, and 1 gram compressed yeast, taken per 100 cc. water.

Expt. 2. "70" grape sugar, water 16.0%, 10 grams sugar and

1 gram brewers yeast ( calc. to dry substance) taken per 100 cc. water.

Expt. 3. "70" grape sugar, water 17.8%, 20 grams sugar and 2 grams compressed yeast per 100 cc. water. Fermentation 10 days at 20 to 25° C. Unfermented residue cleared with alumina cream and filtered.

Expt. 4. "80" grape sugar, water 12.5%, 20 grams sugar and 2 grams compressed yeast per 100 cc. water. Fermentation 10 days at 20 to 25° C. Unfermented residue cleared with alumina cream and filtered.

Expt. 5A. Special sugar from the impure liquor remaining after removing commercial dextrose. Water 16.3%. Solution in water made to 20.5° Brix and  $\frac{1}{2}$  grams compressed yeast added per 100 cc. Fermentation was continued for ten days at 20 to 25° C.

Expt. 5B. A portion of the unfermented residue was examined after removal of the alcohol and concentration and the results given under Expt. 5B beyond.

Expt. 5C. The remainder of the unfermented residue was concentrated to 13.2 Brix., cleared with alumina cream and 1 gram yeast per 100 cc. added and allowed to remain 7 days at 20 to 25° C., when it was cleared with alumina cream and filtered.

The following tables epitomize the analytical data for each of the five experiments here summarized. The figures refer to dry substance in all cases.

| Expt. | Dextrose<br>Equivalent<br>K<br>% | Specific Rotary<br>Power<br>S <sub>d</sub> | Nitrogen<br>% | Ash<br>% | Material<br>in<br>100 cc. |
|-------|----------------------------------|--|---------------|----------|---------------------------|
| 1     | 45.4                             | 112.0                                      | .030          | .60      | 8.38                      |
| 2     | 84.3                             |  | .031          | .70      | 8.40                      |
| 3     | 90.0                             |  | .036          | .73      | 16.56                     |
| 4     | 89.5                             |  | .045          | 1.37     | 17.50                     |
| 5     | 88.8                             | 67.2                                       | .062          | 2.20     | 22.14                     |

The determinations of the dextrose equivalent (K) and the specific rotary power (S<sub>d</sub>) in the unfermented residue were made on the unconcentrated material in Experiments 3, 4 and 5A and on the concentrated material in Experiments 1, 2, 5A, 5B and

5C. Concentration was effected on a water bath, under atmospheric pressure. Solids in these residues were determined by mixing with sand drying to constant weight in a vacuum at 90 to 95° C.

The analyses of the unfermented residues in these experiments are summarized in the following table:

| Expt. | K<br>% | Sd<br>° | Nitrogen<br>% | Ash<br>% | Solids in<br>100 cc.<br>grams | In organic matter<br>K<br>% | Sd<br>° |
|-------|--------|---------|---------------|----------|-------------------------------|-----------------------------|---------|
| 1     | 22.3   | 165.7   | .048          | 1.0      | 5.28                          | 22.5                        | 167.4   |
| 2     | 18.8   | 31.1    | .137          | 3.2      | 1.85                          | 19.4                        | 32.1    |
| 3     | 20.7   | 29.9    | 1.062         | 5.1      | 2.51                          | 21.8                        | 31.5    |
| 4     | 21.6   | 14.1    | 1.139         | 13.0     | 2.07                          | 24.8                        | 16.2    |
| 5-a   | 25.3   | 40.0    | .336          | 10.8     | 4.37                          | 28.3                        | 44.8    |
| 5-b   | 25.4   | 39.5    | .336          | 10.8     | 14.21                         | 28.4                        | 44.3    |
| 5-c   | 25.8   | 40.6    | .288          | 11.3     | 15.37                         | 29.1                        | 45.8    |

From the unfermentable residue obtained in Experiment 5C an osazone was prepared according to the method of Fischer (Ber. 23-3687). No precipitate appeared in the hot liquor, indicating that all the dextrose had been fermented. On cooling the solution, a considerable quantity of an osazone separated out and this was recrystallized four times from water. Its crystalline form throughout consisted of aggregates of fine yellow needles. The melting point of the final product was 120°. The crystalline form agrees with that reported by Fischer (Ber. 23-3687) and Ost (Ch. Z. 20. 762). Fischer found the melting point to be 158°; Ost found 140°-155°, Brown and Morris, Ling and Baker and Ost found that a mixture of maltose and dextrin gave an osazone having a melting point much lower than that of pure maltosazone. It seems probable that the low melting point of the osazone prepared in this experiment is due to the presence of impurities not dextrans because of their low rotation values, but more probably some of the caramelization products of the sugars.

While all of the above experiments were made with equal care, Expt. No. 5 must be considered as the most reliable, for several reasons. In the first place completeness of fermentation was assured by further treatment of a portion of the unfermented



residue with fresh yeast. (Expt. 5C). Then, further, there was found no more nitrogenous matter in the residue than could be accounted for by the amount present in the original material, while in Expts. 3 and 4 the large amount of yeast used apparently introduced some soluble nitrogenous matter into the unfermented residue, while in Expts. 1 and 2 no determinations of nitrogen in the residue were made.

It will be observed that seven days further fermentation of the residue in Expt. 5A did not change the character of the residue as is shown in the results in Expt. 5B. It is also very interesting to observe that there was very little difference even in the constants of the dialyzed material. A little nitrogenous matter was removed, a slight excess of ash introduced and the values for K and  $S_d$  very slightly increased.

The fact that no precipitate separated from the hot solution proves that no more than minute traces of dextrose remained in the unfermented residue. The melting point of the osazone was so low that no appreciable quantity of maltose could be present. These considerations taken in connection with the low optical activity of the unfermented residue point to the presence of a reducing matter which cannot be accounted for by any mixture of maltose or dextrose with dextrin.

The melting point and crystalline form of the osazone make it appear highly probable that the isomaltose prepared by Fischer occurs in some of the more completely hydrolyzed products of starch, such as grape sugar, and possibly in liquid glucose. But before this point can be definitely established, the nature of the substances which occur with the isomaltose in the unfermentable residue must be determined.





# A STUDY OF SOME OF THE PHYSICAL PROPERTIES OF STARCHES

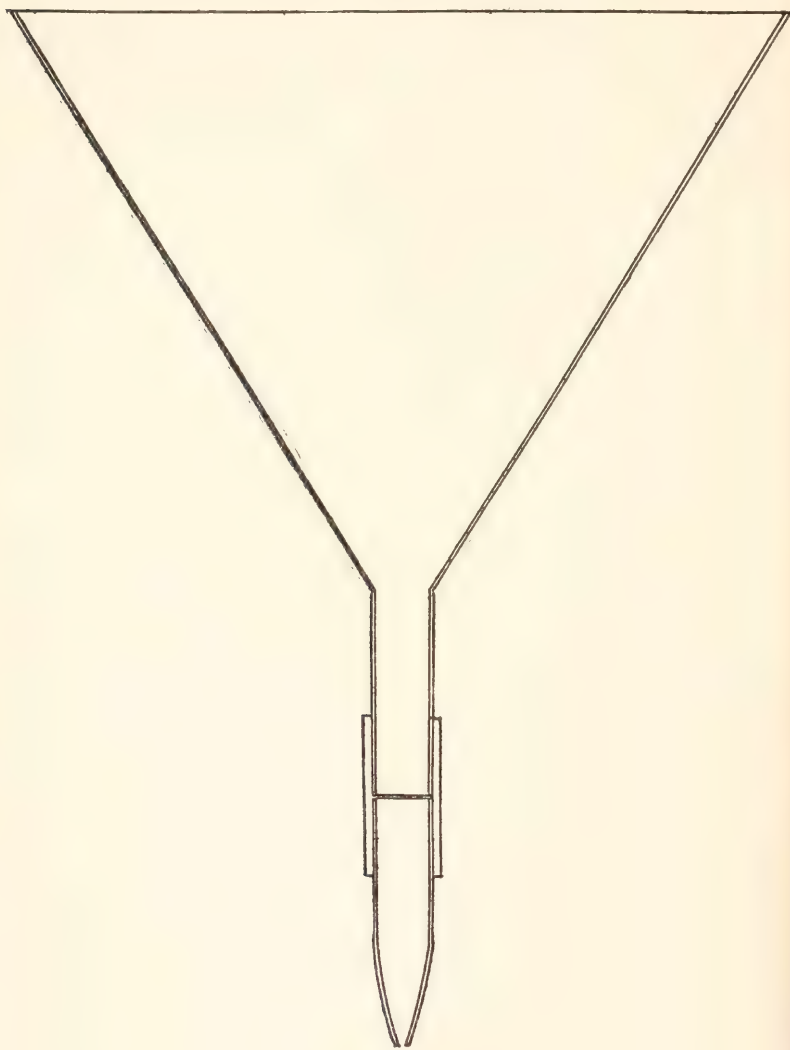
BY HAMBDEN BUEL

*Cliffside, N. J.*

In the manufacture of starches to satisfy the various trade industries both the producer and the consumer have long endeavored to evolve some method of testing the starch which would determine at once its suitability for any or some specified use. The consumer usually has but one usage to contend with, while the producer is confronted with almost endless applications.

The methods which are most generally used are those which aim at an expression of the consistency of the starch paste. To arrive at such an expression in known terms which may at the same time be comparable, different experimenters have devised numberless methods with almost as many varying results. These methods may be roughly divided into three general classes, viz., first, those which measure the resistance to the movement of a suspended body in a given paste; second, those which either measure the ability of a given paste to support a known weight on an examination of the body consistency; and third, those which measure the flow of a given paste. While these methods considered individually may show some very interesting results, when compared with one another they will almost invariably show more or less discrepancy. This discrepancy the author believes may generally be traced to an oversight in properly standardizing the instrument used.

A few years ago the author had occasion to investigate some of these various methods with the point in view of fixing upon one which would be accurate and easily manipulated and at the same time be applicable to the various types and grades of starches with consideration for the properties desired in their different applications. The method then in use was a very simple one, but not very carefully worked out, but exceedingly easy of manipulation. It was this latter point that finally fixed its adoption, after the several defects had been corrected.



*Fig. 1*  
*Scale -  $\frac{3}{4}$ " = 1"*

The method in brief is one of the third type heretofore mentioned and for convenience in future discussion will be designated as the C. P. R. method. The instrument consists of a glass funnel with the stem cut off at a given length and a glass tip connected with a piece of rubber tubing, see Fig. 1. This manner of connecting the tip was to facilitate the cleaning when used for a heavy paste. No provision for temperature control in the instrument itself has been made as the paste is tested as soon as transferred, the funnel having just previously been rinsed in water of the desired temperature. The instruments are first regulated so that they will deliver 105 cc. of water in 70 seconds starting with 125 cc. at 25 degrees C. This determination of the water value is only a preliminary step, the actual standardization being carried out by the use of starches giving pastes of varying consistencies, which consistency has been accurately determined with a funnel and tip which is preserved as a "master instrument" and by which all other instruments are controlled.

The method used is as follows: Five grammes of starch is weighed into a 250 cc. beaker and brought into suspension with 10 cc. of water, then 90 cc. of a 1% sodium hydroxide solution of 25 degrees C. is added and the whole stirred for three minutes at the rate of 70 to 80 R.P.M. The beaker is then placed in a water bath for thirty minutes in which a constant temperature of 25 degrees C. is maintained. About twenty seconds before the expiration of the full thirty minutes the beaker is removed and the starch paste is poured into the instrument and a 100 cc. graduated cylinder is brought under the delivery point by a very short and quick movement at the expiration of the thirty minutes. At the end of seventy seconds the graduated cylinder is removed and the reading in cc. represent the observed fluidity. This observed fluidity is then corrected by means of a curve which is made out for each instrument. A stop-watch is always used in connection with these determinations.

The sodium hydroxide method is employed because it may be more accurately controlled at the critical points than can the aqueous paste method, and the temperature of 25 degrees C. is used because it is nearer a mean temperature for a laboratory, year in and year out.

In order to insure the greatest accuracy in the method it was necessary to determine the essential controlling factors, which were found to be as follows:

First: the strength of the sodium hydroxide solution used.

|                        | %                       | %   | %                        | %    | %    | %         |
|------------------------|-------------------------|-----|--------------------------|------|------|-----------|
| Strength of NaOH sol.  | .5                      | .8  | .9                       | 1.   | 2.   | 3.        |
| Weight of starch — gr. | 5.                      | 5.  | 5.                       | 5.   | 5.   | 5.        |
| CC. of water used      | 10.                     | 10. | 10.                      | 10.  | 10.  | 10.       |
| CC. of NaOH sol. used  | 90.                     | 90. | 90.                      | 90.  | 90.  | 90.       |
| Fluidity as determined | Would not<br>gelatanize |     | Partially<br>gelatanized | 34.1 | 34.0 | 53.5 54.2 |

Second: The effect of variations in temperature. In this as well as in the remaining tests the quantities of starch, water and NaOH sol. was the same as called for in the description of the method, the same starch being used throughout.

| Temperature | Fluidity |
|-------------|----------|
| 15.° C.     | 23.9     |
| 25.° C.     | 34.0     |
| 35.° C.     | 45.2     |

Third: The time the mixture should be allowed to stand.

|                           |               |
|---------------------------|---------------|
| After standing 15 minutes | 29.4 Fluidity |
| After standing 30 minutes | 34.1 Fluidity |
| After standing 45 minutes | 35.7 Fluidity |

Fourth: The effect of the rate of stirring.

| R. P. M. | Fluidity |
|----------|----------|
| 75       | 34.0     |
| 150      | 37.8     |

As the foregoing experiments covered all of the manipulations under which the test is made it was decided to use the constants as given in an earlier paragraph describing the method. These constants, as will readily be seen, may all be controlled with great accuracy and with a minimum of effort.

Having disposed of the question of the controlling factors the next points that came up were the comparative results of different instruments and of different operators. It was very soon found to be practically impossible to construct different instruments that would give identical results, so it was decided to standardize all future instruments according to one preserved as a "master



instrument." This solution of the problem turned out to be very satisfactory as may be seen from the results given in Table 1. This table shows both the comparative results of different operators and different instruments.

TABLE 1

| Operator Instrument      | Corrected Fluidity |      |      |
|--------------------------|--------------------|------|------|
|                          | A 23               | B 23 | C 12 |
| Starch No. 1 (ordinary)  | 1.7                |      | 2.2  |
| Starch No. 2 (modified)  | 17.3               | 17.7 | 17.6 |
| Starch No. 3 (modified)  | 33.5               | 33.1 | 31.0 |
| Starch No. 4 (modified)  | 39.6               | 39.7 | 39.2 |
| Starch No. 5 (modified)  | 48.5               | 48.8 | 49.3 |
| Starch No. 6 (modified)  | 62.6               | 61.8 | 60.3 |
| Starch No. 7 (modified)  | 74.5               | 73.2 | 75.5 |
| Starch No. 8 (modified)  | 81.0               |      | 82.4 |
| Starch No. 9 (modified)  | 90.0               |      | 90.1 |
| Starch No. 10 (modified) | 20.9               | 21.0 | 21.1 |
| Starch No. 11 (modified) | 39.5               | 40.0 | 40.1 |
| Starch No. 12 (modified) | 50.0               | 49.5 | 50.0 |
| Starch No. 13 (modified) | 62.6               | 62.0 | 62.3 |

This table shows very liberally the range of variations of different operators using different instruments. As the full investigation embraces the work on upward of forty instruments and nearly twenty operators, most of whom were connected with different and independent laboratories, a tabulation of the complete results would entail too much space for the purposes of this paper.

TABLE 2

Showing the standardization of the instruments.

| Instrument Operator     | Observed Fluidity |      |        |      |        |      |              |
|-------------------------|-------------------|------|--------|------|--------|------|--------------|
|                         | No. 32            |      | No. 33 |      | No. 34 |      | Master Inst. |
|                         | A                 | B    | A      | B    | A      | B    |              |
| Starch No. 1 (ordinary) | 2.1               | 2.2  | 2.1    | 1.9  | 3.4    | 3.3  | 1.6          |
| Starch No. 2 (modified) | 20.2              | 20.5 | 19.0   | 19.5 | 25.2   | 25.0 | 16.9         |
| Starch No. 3 (modified) | 35.3              | 36.3 | 33.5   | 36.0 | 46.9   | 46.7 | 30.1         |
| Starch No. 4 (modified) | 44.4              | 45.0 | 41.7   | 42.5 | 57.0   | 57.8 | 37.3         |
| Starch No. 5 (modified) | 54.2              | 54.3 | 52.0   | 52.7 | 68.2   | 68.4 | 46.5         |
| Starch No. 6 (modified) | 67.0              | 67.0 | 65.2   | 65.0 | 80.3   | 79.5 | 60.6         |
| Starch No. 7 (modified) | 82.9              | 83.7 | 81.1   | 81.2 | 91.0   | 91.0 | 78.7         |
| Starch No. 8 (modified) | 86.9              | 86.8 | 85.5   | 85.2 | 93.2   | 93.3 | 82.9         |
| Starch No. 9 (modified) | 92.3              | 94.0 | 90.8   | 91.8 | 96.1   | 95.6 | 89.7         |

The correction curve is then plotted from the figures thus obtained in Table 2. The fluidity as shown by the "master instrument" is taken as the standard and the average results of the two operators on each instrument are taken from the points of the curve for that instrument. The correction curves for the above three instruments are shown in Figure 2.

The next matter to come up for consideration was the comparative results with different types of instruments.

The first one was that used by a large starch consumer. This instrument was in the shape of a long cylinder about one inch in diameter and fifteen inches long, the lower end of which was drawn out to a small orifice and having zero and 100 cc. marks about nine inches and three inches from the bottom respectively. A glass rod with a ground seat extending down on the inside of the tube was used to start and stop the flow. The sodium hydroxide paste is used and the results show the time required for the delivery of 100 cc., which is the reverse of the results by the C.P.R. method.

These instruments were only standardized to a water value and the error in not further and more thoroughly standardizing them may be seen from the results shown in Table 3.

TABLE 3

| Instrument                    | Blank        | Viscosity<br>No. 3 | No. 6       |
|-------------------------------|--------------|--------------------|-------------|
| Water                         | 38 3/5 sec.  | 38 2/5 sec.        | 38 2/5 sec. |
| Starch No. 1, C.P.R. fluidity |              |                    |             |
| 51.0                          | 60 2/5 sec.  | 74 1/5 sec.        | 49 sec.     |
| Starch No. 2, C.P.R. fluidity |              |                    |             |
| 21.0                          | 101 2/5 sec. | 144 1/5 sec.       | 74 4/5 sec. |
| Starch No. 3, C.P.R. fluidity |              |                    |             |
| 49.0                          | 63 2/5 sec.  | 77 4/5 sec.        | 50 sec.     |

Subsequent work with these instruments embracing upward of 200 determinations showed that after the starch value had been properly determined the results were quite consistent.

The next instrument taken up was the Doolittle Tortion Viscosimeter. This method makes use of an aqueous paste and the comparative results may be seen in Table 4. The values of this instrument are the reverse of those indicated by the C.P.R. method.

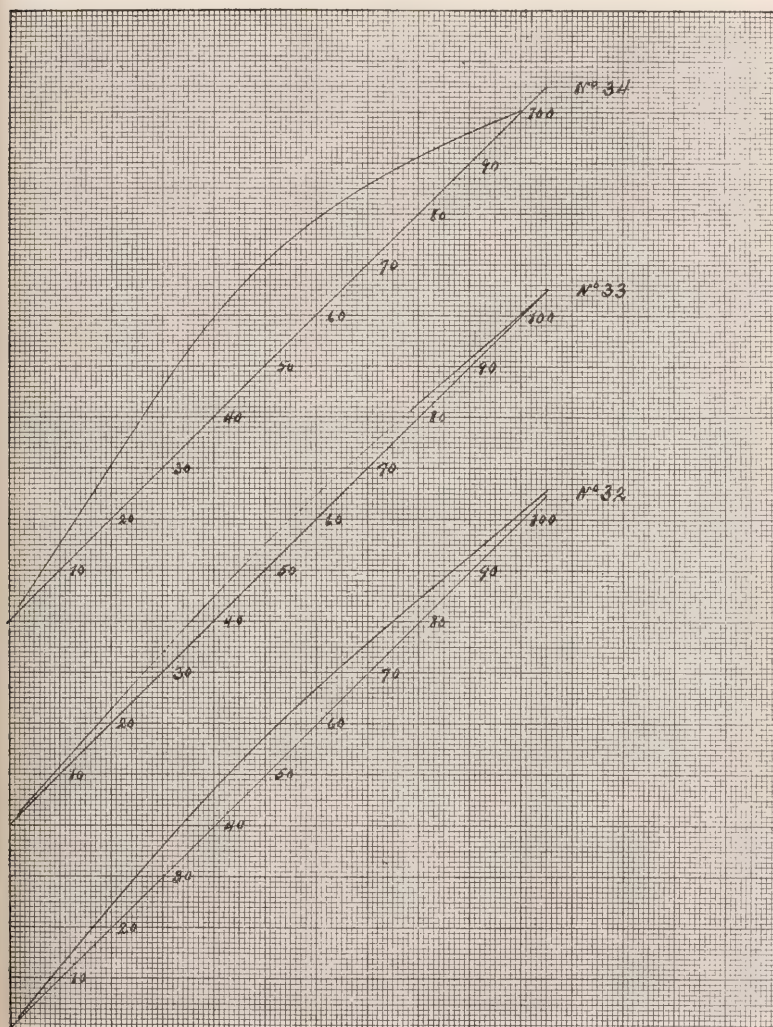


Fig. 2.

TABLE 4

|                | C. P. R. Fluidity | Doolittle Viscosity<br>Too thick to test |
|----------------|-------------------|--|
| Starch No. 192 | 13.0              |  |
| Starch No. 194 | 18.5              | 100.                                     |
| Starch No. 195 | 20.6              | 99.                                      |
| Starch No. 193 | 21.2              | 98.4                                     |
| Starch No. 198 | 36.8              | 84.9                                     |
| Starch No. 191 | 48.6              | 75.8                                     |
| Starch No. 199 | 54.5              | 74.5                                     |
| Starch No. 203 | 57.5              | 70.7                                     |
| Starch No. 204 | 58.1              | 71.5                                     |
| Starch No. 200 | 67.1              | 64.7                                     |

The Doolittle Viscosimeter is a very well constructed and standardized instrument. However, when it is employed for the determination of viscosities in starch pastes it cannot be used without varying the strength of the pastes for widely different starches. For instance, the quantity of the soluble or highly modified starch that would be required to give a paste of the proper consistency for using with the instrument would give an entirely too stiff a paste with a thick boiling starch. In an effort to overcome this objection experiments were made with wires of different sizes, but without any very satisfactory results. As to the manipulations, these were not nearly so simple or easily controlled as in the C.P.R. method. One very serious objection was the corrosion of the delicate wire. Although the instrument was kept in a special glass case, it was found that the wire would slowly become weaker, which fact would necessitate a restandardization from time to time.

Three other methods were also tried, viz.: first, the Rustless Nickel Steel Viscosimeter; second, one proposing to determine the ability of a given paste to support a known weight; and third, a method proposed by Dr. Th. Breyer of Chicago.

The first of these methods consists of a copper water jacket about nine inches in diameter and five inches deep, in which is fixed a heavy nickel-steel cup holding about 300 cc. with a small orifice tube about one inch long screwed in at the bottom and projecting upon the inside of the cup about half an inch. These orifice tubes may be procured in different sizes. Either the sodium



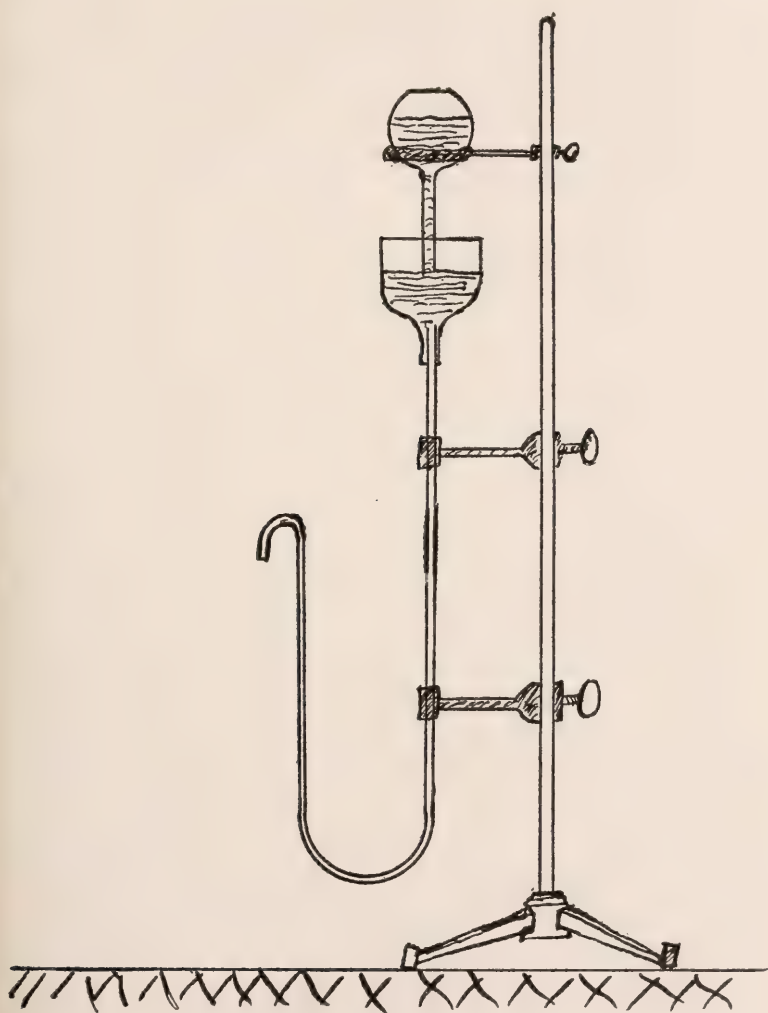


Fig. 3      Scale 1" = 5"



hydroxide or aqueous paste may be used with the instrument, but it was found that the orifice tubes of supposedly the same size did not give corresponding results and would therefore have to be standardized as in the C.P.R. method. Furthermore, it was not so easy to handle as the latter.

In the second method there were found to be two chief objections. First, the great difficulty of controlling the important factors in preparing the paste. Second, in working with starches of widely different characters it necessitated a preliminary test in order to determine approximately the quantity of starch to be used to give a paste of the desired consistency.

The method proposed by Dr. Breyer is extremely unique and possesses one important advantage in that it provides for a constant head. See Figure 3. The main part of this instrument, the long bent glass tube, is made from barometer tubing of specified diameter. The construction of the instrument in its main features is rather delicate and is hardly capable of being quickly cleaned. Furthermore, because of the great length of the small glass tube, which is essential since it depends upon the skin friction of a thin solution, should be provided with a constant temperature jacket, because the time required for the solution to traverse the full length, in conjunction with the small volume, makes it very susceptible to slightly varying changes in temperature. This instrument will permit the use of either the sodium hydroxide or aqueous pastes and when corrected for the above-mentioned defects and properly standardized might prove to be exceedingly valuable.

In conjunction with the regular tests by the C.P.R. method there has been carried on a very simple check test. This "check test" consists of simply boiling a given weight of starch in a given amount of water for a fixed time and transferring same to a funnel with a tuft of cotton in the apex and covering the funnel with a piece of paper, and setting aside over night at room temperature. The following morning the starch jelly is shaken out from the funnel and its consistency examined by hand and the comparative results noted along side that of the determined fluidity. These comparative results have embraced all types and grades of starches and cover upward of two thousand determinations.

The results of these comparative tests mentioned in the foregoing paragraph have shown the determinations as made by the C.P.R. method to be highly consistent. It should be noted here that it is not the intention to critically compare the consistency of one type of starch with that of another except in a general way. Extensive investigations have shown that the different types such as corn, cassava, potato, rice, wheat, etc., each have their own distinctive characteristics. Starches of different types, but of the same fluidity, usually produce pastes of widely different characters, *i.e.*, a wheat would give a paste of a mush-like consistency, while potato would give a paste more gum-like, whereas that of corn would be between the two. Furthermore these characteristics might be varied to a certain extent by the manner of preparation, such as in the time of cooking, stirring, standing, etc.

In an earlier part of this paper it was stated that the C.P.R. instrument was first regulated to a specified water delivery using 125 cc. of water, while the actual fluidity determinations are carried out with 100 cc. of solution plus the weight of the starch used. It will, of course, be seen that the head will be variable with the different fluidity starches. This latter point, which in itself would be serious, becomes practically negligible when it is considered that each instrument is standardized against a "master instrument" for different fluidity starches and the corresponding correction curve will reduce all results to a common basis. The actual use of these instruments in regular daily control work in producing uniform starches constitutes after all their highest endorsement.

Further experiments along different lines showed numerous inherent peculiarities, chief of which may be mentioned in brief, as follows:

First: It was observed that modified starches of an acid character usually showed an increasing fluidity with age varying from 4 to 10 points in the lapse of five months.

Second: The aqueous paste tests were shown to be susceptible to variations in the time of cooking as follows:

| Time cooked | Fluidity |
|-------------|----------|
| 3 minutes   | 42.5     |
| 4 minutes   | 15.0     |
| 5 minutes   | 7.5      |
| 7 minutes   | 4.0      |
| 10 minutes  | 3.0      |

This was also a variable quantity with the different types of starches.

Third: The aqueous paste tests when prepared and cooked in the same way showed varying fluidities when allowed to stand different lengths of time, to wit:

| Time cooked | Time cooled        | Fluidity |
|-------------|--------------------|----------|
| 3 minutes   | 1 hour             | 23.0     |
| 3 minutes   | 2 hours            | 16.5     |
| 3 minutes   | 3 hours            | 4.5      |
| 3 minutes   | 6 hours            | .2       |
| 5 minutes   | $\frac{1}{2}$ hour | 10.0     |
| 5 minutes   | 1 hour             | 4.0      |
| 5 minutes   | 4 hours            | 6 drops  |

Fourth: A large sample of starch was divided into nine parts and dried at low temperature to different moisture content and the fluidities determined with the following results:

| Moisture              | Fluidity |
|-----------------------|----------|
| 16.66 original sample | 72.7     |
| 13.51                 | 70.7     |
| 12.76                 | 69.8     |
| 12.07                 | 69.6     |
| 11.10                 | 69.3     |
| 10.30                 | 69.0     |
| 6.90                  | 67.3     |
| 4.00                  | 66.2     |
| .30                   | 63.4     |

This experiment in reality shows the relationship of fluidity to dry substance.

Fifth: Different types and grades of dry starches were exposed under varying conditions of time and humidity, but no especially interesting results were obtained, though some starches did differ from others as to the amount of moisture they would take up.

There are several agents when present in a starch influences its character to a greater or less degree. Acids will cause a liquefaction in the starch paste, while alkalis and borax will usually

produce a stiffening effect when present in a certain amount. Lastly a starch may have become contaminated with micro-organisms at some point or other of its manufacture or handling, and contain very resistant spores of a form that develops diastatic enzymes. Such forms, of course, will have a liquifying action upon a starch paste, which action may not become apparent until after the starch has stood several hours.

In the general question of paste consistency there are two points that it might be well to bear in mind; first, whether it would be best that the method should be applicable to all starches for a given purpose; or second, whether it should be applicable to all starches irrespective of any particular use. In other words, should it have a narrow or broad application?

If it were possible to devise a method for the narrower application, as for instance the determination of the suitability of any particular starch for laundry purposes it would be very well, but this is hardly apt to be realized. There are too many individual characteristics in starches that act differently under the various conditions. Not long since one very large user of laundry starch, who was using a Doolittle instrument with considerable satisfaction, was confronted with a starch which his test would have condemned, but subsequent use in the laundry proved it to be highly satisfactory.

The real value of a consistency test might prove of greater worth if it were perfected in line with the broader application. Worked out along this line it should be regarded with due consideration of the individual characteristics of the particular starch to be tested, its intended use, and the conditions affecting its use. For instance, a laundry has been using a wheat starch for certain purposes having a fluidity of say 50. As long as it uses this particular type of starch the simple consistency test may be sufficient to determine its value. But suppose that the laundry be given a corn or potato starch of the same fluidity, it would probably be found that the standard used for wheat would be incorrect if applied to the corn or potato starch, although other grades of these two latter starches might give equal satisfaction.

An additional property of starches and one not heretofore emphasized, but which may be found to play a very important

part in their application to various usages, is that of cohesion. A close study of this property may reveal some very interesting facts.

In connection with some of the work herein cited the author wishes to acknowledge his indebtedness to H. C. Humphrey and Chr. E. G. Porst for several valuable suggestions.



## SCIENTIFIC CONTROL OF SULPHITE PULP MANUFACTURE

BY CHARLES M. BULLARD

*Boston, Mass.*

In the year 1884, at Rumford, R. I., the first sulphite mill in America was built and operated by the Richmond Paper Company. Since that time there have been built 102 sulphite mills in America of approximately 5200 tons daily capacity in bleached and unbleached sulphite fibre.

To produce this enormous amount of fibre, it is safe to say that approximately 12,000 cords of wood, 1,500,000 lbs. of sulphur and 1,200,000 lbs. of lime and its equivalent in limestone is used per 24 hours, or an average of  $2\frac{1}{4}$  cords of unpeeled wood, 280 lbs. of sulphur, and 235 lbs. of lime per ton of product.

In discussing the various phases of sulphite manufacture, this paper will deal with the unbleached product on'y, and to determine the amounts of raw materials used on a bleached basis it is safe to add 10% to any figures given.

The most expensive raw material entering into the manufacture of sulphite pulp is wood. Its price varies greatly in different localities and under varying conditions and is steadily advancing from year to year. It is safe to say, however, that it will not average less than \$8.00 per cord, and that an average of  $2\frac{1}{4}$  cords is used per ton of sulphite produced. Figuring on this basis the total amount of wood used is costing the mills approximately \$96,000 per 24 hours or \$18.00 per ton of product.

The next expensive raw material is sulphur. Its price varies but slightly for different localities and averages \$23.00 per ton, therefore the mills will spend about \$18,000 per 24 hours for this material, or on a tonnage basis their sulphur is costing them \$3.64 per ton of sulphite.

Lime is the cheapest material used and its average cost is 30c. per hundred. The average amount used is 235 lbs. per ton,

therefore this material is costing the mills \$3600 per 24 hours or about 71c. per ton of product.

The users of sulphite today are demanding more and more as regards strength, color and cleanliness, and to meet this demand and still make a fair margin of profit the manufacturers must necessarily reduce the cost of production in every possible way, as their profit does not so much depend on the market price, which is fairly stable, as on the cost of production.

The manufacturers do not appreciate the countless ways where scientific control of every stage of the sulphite process will surely aid them to reduce this cost, and still maintain or improve the quality of production, and the sooner they realize that the old "rule of thumb method" so much in vogue in the past should be supplemented by the latest and most improved methods, the sooner they will be enabled to pay greater dividends and still compete with European manufacturers, where the cost of labor and raw material is much lower than in America, and especially in the United States.

The lack of scientific control and failure to make use of scientific methods in the average mill is the direct cause for the needless expenditure of large sums of money during the process, for such results as they are getting, both as to cost of production and quality of product, and were they to skillfully compare their operations in every stage of the process and the results therefrom with those of the few who have applied scientific methods and given them a fair trial, they would at once appreciate the value of these methods.

A very few have made use of these methods and control in their lumbering operations and by so doing have demonstrated its value. In the majority of cases, however, these operations are costing the manufacturers or operators excessively in labor, but what is of equal or more importance is the question of wood waste.

The writer has seen many instances where this waste was enormous. Large quantities of available and valuable wood in the form of tops and large limbs are left scattered broadcast, which are a menace to standing timber from fire. Another large loss is due to not cutting close enough to the ground and many tons are unskillfully felled in inaccessible places where they are

left to decay. These losses are mainly due to the lack of appreciation of what could be saved were these operations scientifically controlled.

In the handling, storage, and delivery of wood to and through the wood room, it is remarkable what can be done in many mills by carefully studying their individual needs and conditions. In one instance out of many, the wood room cost \$1.37 per ton. Their needs and conditions were carefully studied and various changes made in apparatus and methods, with the result that more wood is being handled with less labor and waste, at a cost of 61c. per ton, and there is still room for improvement.

A good deal of argument has come up from time to time as to which was the more economical method for barking wood, to peel it in the woods during the peeling season or at the mill by the usual mechanical method. It would seem that the former method was to be generally favored as the loss is about 9% as against an average of 25% by mechanical barking, and in many instances will run much higher.

The former method will certainly allow much more thorough and uniform drying or seasoning, which is highly important, and when the wood is delivered to the mills by rail and the freight charged by weight as is usual, we should expect a very large saving in the first cost of wood.

Wherever wood is being barked at the mill by the usual mechanical method (by the use of the ordinary disc barker) the use of scientific methods will show very large savings in wood wastes and increased capacity of wood room. Many careful tests made by weight have shown the loss during this operation to run as high as 30%, when under proper conditions this should not run over 21%, and in some instances even less. Such conditions actually exist, and the savings which it is possible to make are therefore very apparent.

A very recent instance of what can be done in this direction will serve to illustrate the value of proper control of the barking operations. A mill was barking approximately 200 cords of wood per day. Careful tests made by weight showed a loss of 28½% during this operation. Various inexpensive changes were made, principally by changing the speed at which the stick was turned while in contact with the barker disc, increasing the speed of the

disc, decreasing the set of the barker knives, and then tests made showed the loss to be reduced to 22%, or a saving of  $6\frac{1}{2}\%$ , equivalent to 13 cords saved per 24 hours.

The yield per cord and quality of fibre is very largely controlled by the uniformity of chips produced, and this uniformity, as well as the amount of sawdust and sulphite screenings (which are a direct loss) are directly controlled by the conditions of the chipper, its speed and the manner of supplying the wood to it. The average amount of sawdust, which is a clear loss, is not less than 5% of all wood chipped, while the sulphite screenings will not average less than 5%. In the majority of cases these two losses can be reduced 40% by scientifically controlling the chipping operation, which when done represents an enormous saving to the manufacturers.

Very recently a mill was chipping wood for 50 tons production. Careful and exhaustive tests were made to determine the uniformity of chips produced, and the amount of sawdust made. The amount of sawdust was found to be averaging between 6 and 7% and a slightly larger amount of course chips, slivers and large pieces of uncut wood were formed, which on entering the digesters with the good chips were scarcely if any affected by the acid during the cooking operation, and eventually were lost as screenings.

Careful attention was given to the condition of the chipper as regards grinding and setting of the cutting knives, face plates and bed knife. The speed was then changed and the men attending the chipper instructed as to the best method of delivering the wood to it. After these changes were made, other careful tests showed the loss in sawdust to be reduced 51% and the large chips and uncut wood, which eventually turned up as screenings, were reduced 46%. This represents a very large saving in wood and increased yield per cord.

The acid plant is the heart and nerve center of a sulphite mill, and is usually the most neglected department. At no stage of the whole sulphite process will scientific methods and control show greater return than here.

Many manufacturers seem to think that any one who can shovel sulphur into a burner at his own discretion is fully capable



of handling this very important operation economically and efficiently. They apparently do not appreciate the superiority of one type of burner over another, the requisite amount of burning area which should be available for the greatest economy, the most efficient draft to carry on them under varying conditions, and the best method for supplying or feeding sulphur to them. Many, and I may say the majority, do not seem to realize that without proper air and temperate control in the burners, from 5 to 10% of sulphur burned may be oxidized to  $\text{SO}_3$  (nor make any attempt to determine this), which in itself is a direct loss, but later in the operation will cause still more loss in lime from the formation of calcium sulphate. This in turn causes another loss in labor, production and innumerable troubles by the plugging up of pipes, bottoms of digesters and blow-pits, and eventually shows up in the finished product.

The strength and purity of gas produced on entering the acid systems is not given the attention which it demands for the best results and the majority of mills do not even make analysis to determine this. If every manufacturer realized the importance of eliminating every air leak throughout the entire acid making system, properly controlled the temperatures during the various stages of the process, doubled and in many instances trebled the lime slacking capacity, properly introduced and distributed the digester relief in the acid storage and reclaiming tanks, with proper temperature control, they would be astonished at the great improvements in efficiency and economy during the acid making process, as well as the decrease in the consumption of sulphur and lime per thousand gallons of acid made.

It is remarkable how little it takes to demoralize the acid making process which will cause the cost to go up with leaps and bounds, and still how simple and economical this process can be handled by applying scientific methods.

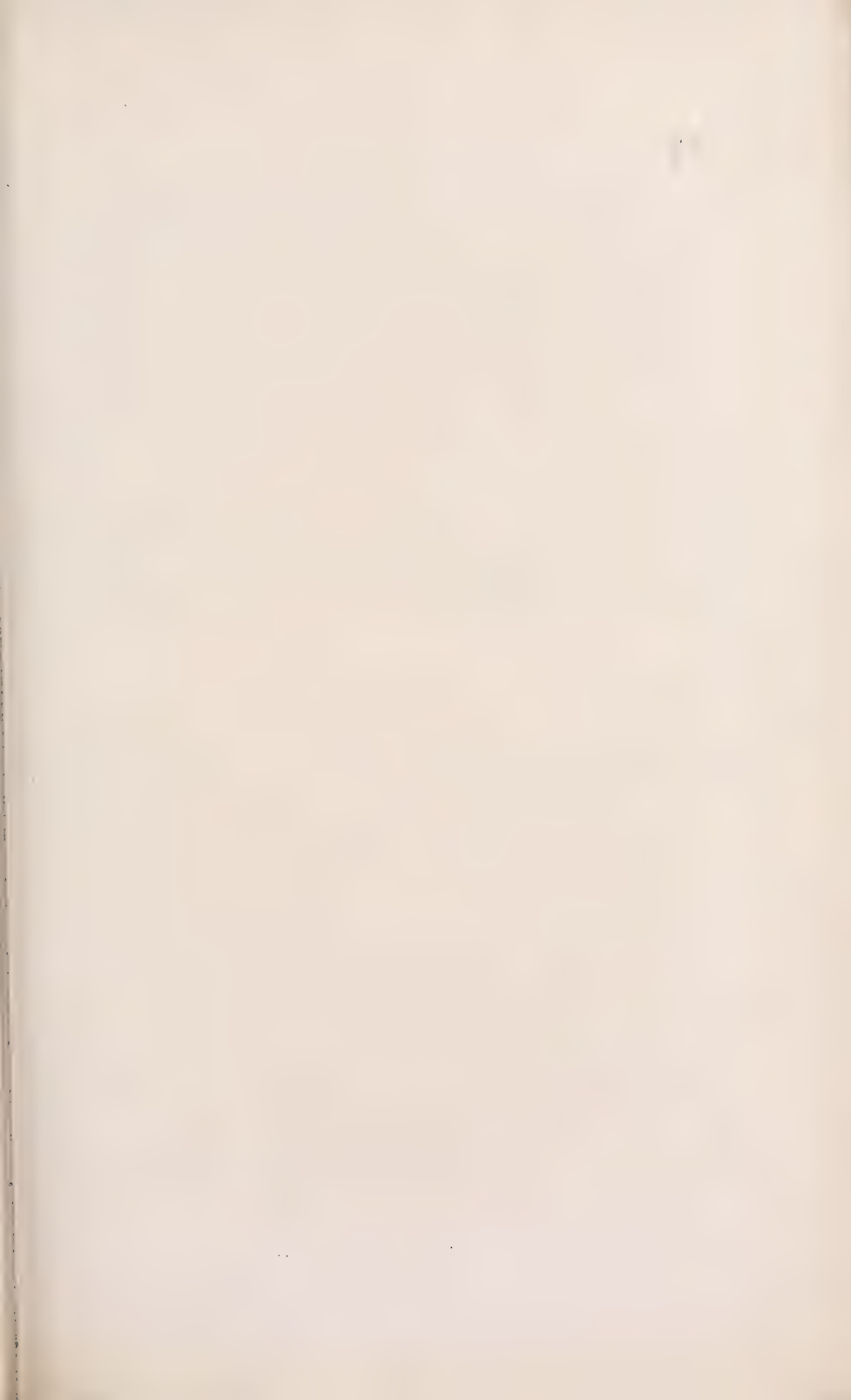
The cooking of wood requires the most careful and uniform control if the best results as regards maximum yield, strength and color are obtained. These results are directly controlled by pressures and temperatures carried in the digesters and manner of relief during this operation, and were the manufacturers to realize this and carry on this cooking operation on a scientific basis, very greatly improved results would be obtained.



Many do not seem to appreciate the ill effects of high temperatures, especially during the first part of the cook, and this being controlled by the relief, directly influences the retention of acid strength during the cook so necessary for the best results.

It is quite impossible to make any set rule as to the exact manner in which every digester should be handled, as conditions vary so widely in different mills, and it is therefore necessary to scientifically study their conditions and needs in order to determine what method should be followed to produce the best results. When this is done, and these methods enforced, the desired results are sure to follow.

In many mills the great variations in quality is the cause for wonder, worry and poor results. On the other hand it is possible to remove or prevent the troubles due to this variation by applying and adhering to improved methods during the cooking process, as there is always a reason for every result obtained whether it be good or poor. The washing, handling and scouring of sulphite is usually considered a purely mechanical proposition and in a large measure this is true, but even here the scientific study of conditions and needs and application of improved methods will almost invariably demonstrate their value in the savings in power, labor and increased efficiency, and its general adoption will be the means, and I may say is the only means of successfully solving the many perplexing problems which are constantly coming up during the whole process of the manufacture of sulphite pulp.



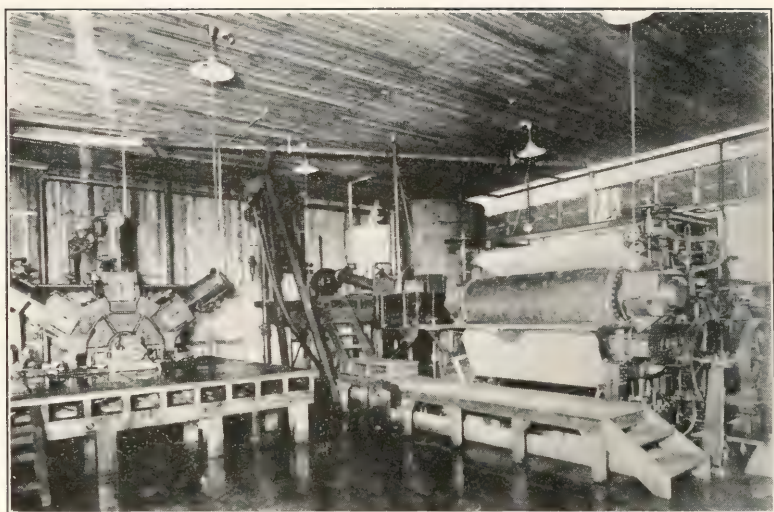


PLATE 1  
Figure 1. VIEW OF GRINDER ROOM

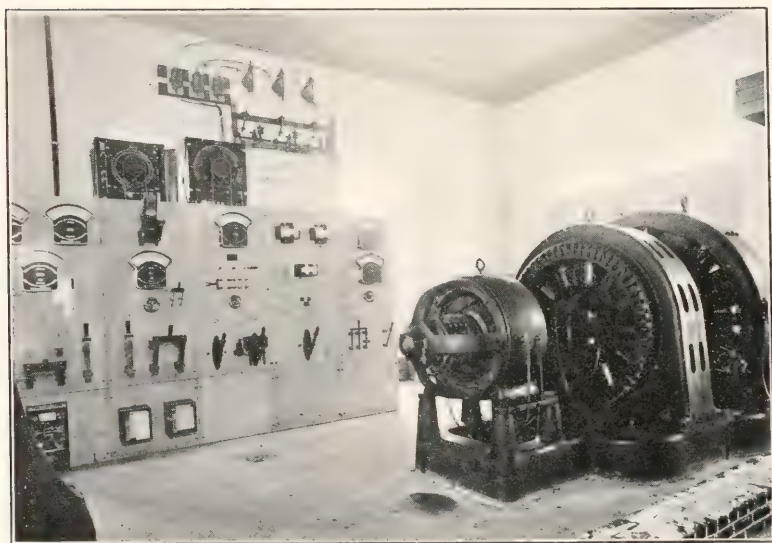


PLATE 1  
Figure 2. A PORTION OF THE ELECTRICAL EQUIPMENT

# THE EFFECT OF VARIABLE GRINDING CONDITIONS ON THE QUALITY AND PRODUCTION OF MECHANICAL PULP

BY MCGARNEY CLINE AND J. H. THICKENS

*Madison, Wisconsin*

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## INTRODUCTION

Briefly stated, mechanical pulp is produced by pressing sections of log against a revolving grindstone, which may or may not be revolving in a pit of moist pulp. If revolving in thick pulp the hot grinding process is employed; if a large excess of water is used the resultant process is one of cold grinding. The factors which enter into the production of mechanical pulp from any species of wood are:

1. The surface of stone; whether rough or smooth, sharp or dull, or of coarse or fine grit.
2. The pressure with which the wood is forced upon the stone.
3. The peripheral speed of the stone.
4. The temperature of grinding.
5. The moisture content, weight per cubic foot, and the condition of the wood to be ground.

As a result of operating under different combinations of these factors (different combinations of surface, pressure, speed, temperature, etc.) certain other resultant factors are developed. These are:

1. The horsepower which must be applied to the grinder.
2. The amount of pulp produced in 24 hours (tons of 2000 pounds).
3. The horsepower consumption per ton of pulp in 24 hours.
4. The yield of pulp and screenings per cord of wood ground.
5. The quality of the pulp.

In commercial practice there is wide variation in the method of producing ground-wood pulp. Its manufacture is generally conducted according to certain rules-of-thumb which have been

developed as a result of long practice. Peculiarly, however, one will hardly find two mills which operate under exactly the same conditions. Each superintendent or manager has his own theories, and, as a result, there are almost as many different methods employed in the manufacture of ground-wood pulp as there are mills. The results obtained from a large number of commercial plants in the United States indicate that the pressure used in grinding varies from 17 pounds per square inch on a 14-inch cylinder to 116 pounds; the peripheral speed from 1360 feet per minute to 4310 feet; the temperature from cold to 153° F., the horsepower connected to a single grinder varies from 135 horsepower in one mill to 625 in another. Likewise the consumption of power per ton of pulp in 24 hours is claimed in one mill as low as 31 horsepower, while in another as high as 125. It is only reasonable to suppose that there is some combination of pressure, speed, power to the grinder, etc., which will give the most efficient and economical results. The experiments upon which this paper is based were carried on for the purpose of determining as accurately as possible the laws underlying the production of mechanical pulp.

#### EQUIPMENT AND METHODS

The equipment used consisted of a swing cut-off saw, a mechanical barker, a commercial-sized 3-pocket grinder taking a stone 54 inches in diameter by 27 inch face, together with the necessary auxiliary pumps, screens, and a wet machine for the removal of water from the pulp. In screening the pulp a centrifugal screen taking a plate perforated with .065 inch holes was used. The screenings from this machine were rescreened in a flat plate screen, the slots of which are .012 inch wide.

The wood grinder was direct connected to a variable speed, direct current motor, the efficiency of which was known for all speeds and loads, thus making possible the exact determination of power applied to the grinder. Calibrated instruments were used in power measurements and graphic records were taken of the power applied to the grinder and of the temperature of grinding.

In the treatment of woods prior to grinding, a steaming tank 3 feet in diameter by 8 feet high was employed. This tank was



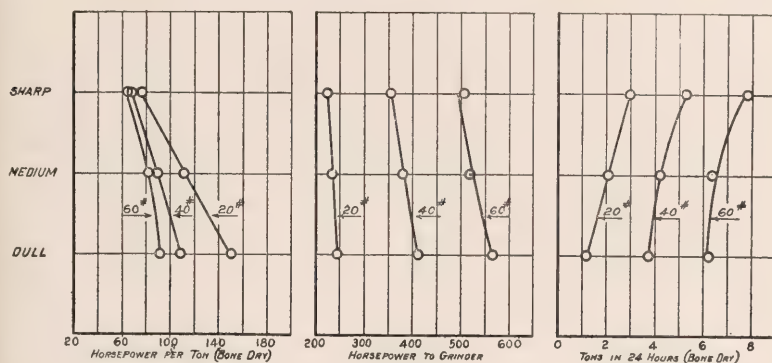


PLATE 2

*Condition of Tests.*

Speed: 225 R. P. M.

Surface: Sharp. 6 to the inch spiral cut (deep grooves).

Medium. 8 to the inch diamond cut (medium depth).

Dull. 3 to the inch straight cut and 12 to the inch spiral cut (shallow grooves).<sup>9</sup>

Process: Hot Grinding.

Pockets used: 3 at a time.

provided with steam vacuum and water connections. Views of a portion of the electrical machinery and the grinder room are given on Plate 1.

The general method of conducting tests was as follows:

The desired surface was placed on the pulpstone by means of a bush roll or burr; and, after measuring the diameter of the stone, an impression was taken of its surface by means of a piece of coated paper and a sheet of carbon paper, this record being later photographed. The wood for the test was sawed into 2-foot lengths, and the bark removed, sections of the wood being taken for the determination of moisture content and bone-dry weight per cubic foot. The stone was cold at the beginning of each test, and the run was continued until approximately 750 pounds of bone-dry wood had been ground. The pulp and screenings obtained were weighed and the moisture content of each determined. During any test the pressure and speed were maintained as nearly constant as possible. The quality of the pulp was recorded by means

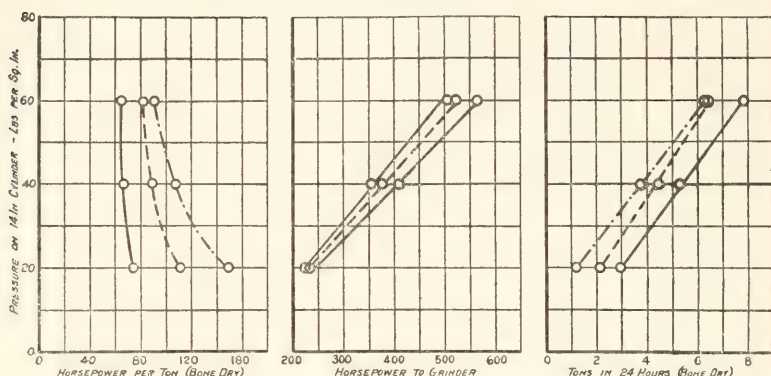


PLATE 4

*Conditions of Tests.*

Speed: 225 R. P. M.

Surface: Full line. 6 to the inch spiral cut.

Dashed line. 8 to the inch diamond cut.

Dash and dot. 3 to the inch straight cut and 12 to the inch spiral.

Process: Hot Grinding.

Pockets used: 3 at a time.

of photomicrographs of the fiber and by manufacturing it into newsprint paper. The samples used in the paper tests were beaten with 20 per cent of bleached spruce sulphite for a period of one hour, then run into a sheet on a 12-inch paper machine. No color, size, alum, or loading was used in making the paper. Tests for color, bursting strength, tensile strength, stretch, etc., were made on the paper samples. This portion of the work has not been completed, however, and the results given are only such as could be deduced from a comparatively small number of tests.

The steaming of wood for tests was carried on for different lengths of time and at different pressures, the condensation being drawn off at frequent intervals. In each case the wood was ground immediately after it was removed from the steamer.

## RESULTS

In analyzing the results of the tests a number of relations have been found to exist, and while some of these do not appear in accordance with the results obtained by other investigators, they

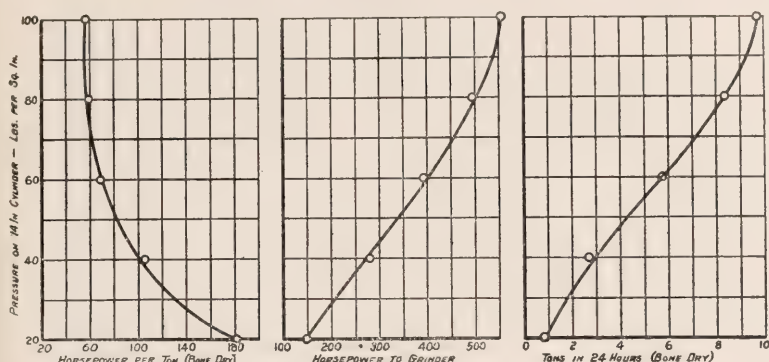


PLATE 5

*Conditions of Tests.*

Speed: 225 R. P. M.

Surface: 3 to the inch straight cut and 12 to the inch spiral.

Pockets used: 2 at a time.

Process: Hot Grinding.

have been tried out commercially and found to be essentially correct.

## SURFACE OF STONE

The "surface of stone" involves several different factors; the size of the sand particles might be the important factor in some cases, the sharpness of grit the important one in others. However, in this series of tests, variations in the surface of the stone were obtained by working the surface of the same stone with steel rolls of different design, thus forming upon the stone depressions of different depths and patterns.

*Horsepower per ton. Horsepower to the grinder.*

*Production in 24 hours.*

Plate 2 shows graphically the relation between the different surfaces of stone and the horsepower consumption per ton, power to the grinder, and production in 24 hours. The curves shown were obtained at pressures of 20, 40, and 60 pounds. It will be noted that the horsepower per ton varies inversely with the degree of sharpness of the stone. The horsepower to the grinder

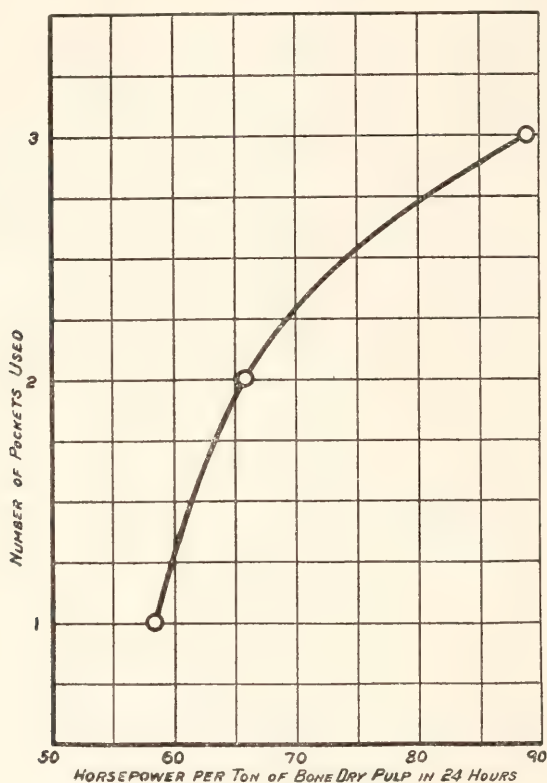


PLATE 6

*Conditions of Tests.*

Speed: 225 R. P. M.

Pressures: One Pocket—120 pounds on 14-inch cylinder.

Two Pockets—59.5 pounds on 14-inch cylinder.

Three Pockets—36.5 pounds on 14-inch cylinder.

Surface: 3 to the inch straight cut and 12 to the inch spiral.

Power to the Grinder: 330 horsepower.

Process: Hot Grinding.

varies in like manner, while the production in 24 hours varies directly with the degree of sharpness.

One thing which is of particular interest is the fact that the curves apparently come together at a point corresponding to



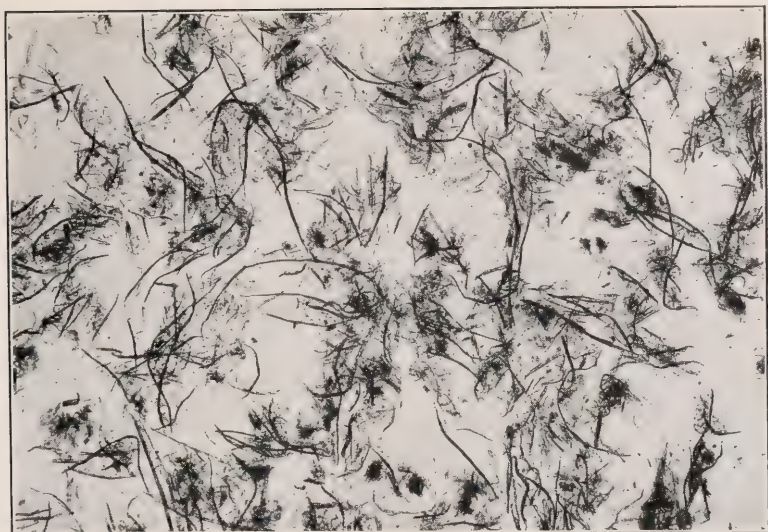


PLATE 3. Figure 1

PHOTOMICROGRAPH SHOWING THE FIBERS OBTAINED ON DULL STONE

Power Consumption:  $84\frac{1}{2}$  horsepower per ton.

Magnification: 15 diameters.

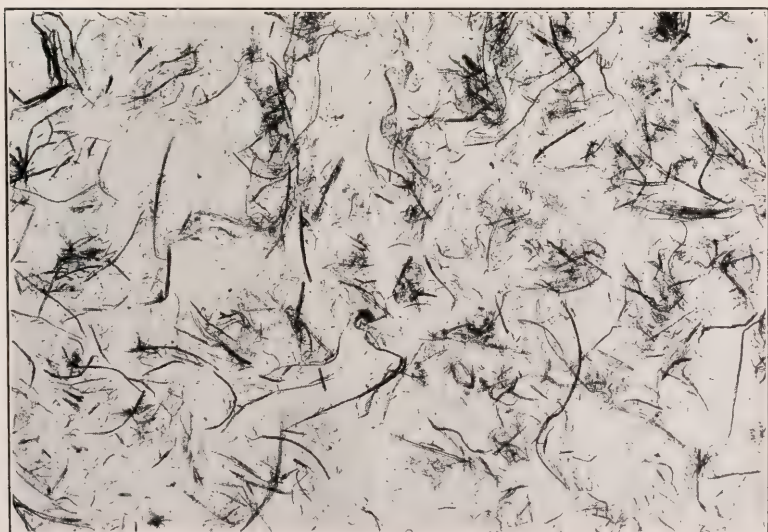


PLATE 3. Figure 2

PHOTOMICROGRAPH SHOWING THE FIBERS OBTAINED ON SHARP STONE

Power Consumption: 64 horsepower per ton.

Magnification: 15 diameters.





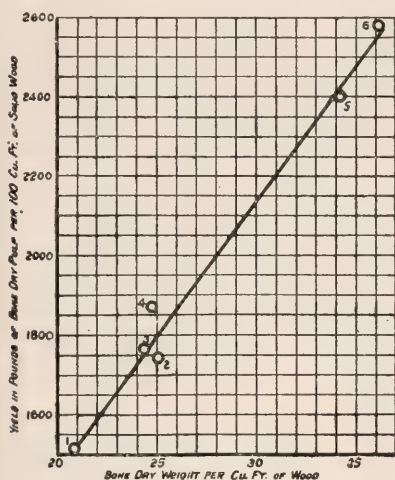


FIGURE 1

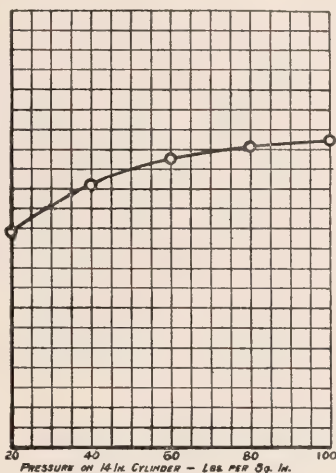


FIGURE 2

## PLATE 7

*Figure 1. Conditions of Tests.*

Speed: 200 R. P. M.  
 Pressure: 40 lbs. on 14<sup>1</sup>/<sub>2</sub> Cylinder.  
 Surface: 3 to the inch straight cut  
 and 12 to the inch spiral.  
 Pockets used: 3 at a time.  
 Process: Hot Grinding.  
 Wood Treatment: Steamed 8 hrs. at  
 60 lbs. pressure.

## Kinds of Woods:

1. Balsam Fir.
2. Hemlock.
3. Jack Pine.
4. Poplar.
5. Tamarack.
6. White Birch.

*Figure 2. Conditions of Tests.*

Speed: 225 R. P. M.  
 Surface: 3 to the inch straight  
 cut and 12 to the inch spiral.  
 Pockets used: 2 at a time.  
 Process: Hot Grinding.

approximately 50 horsepower per ton. This leads one to believe that, regardless of the pressure, it would be impossible with the apparatus used to produce pulp with less than 50 horsepower per ton in 24 hours.

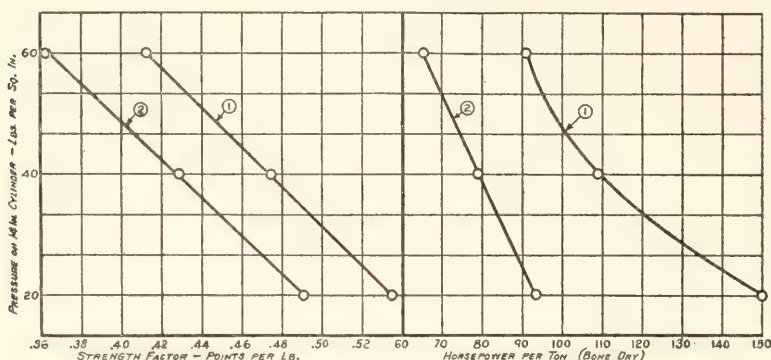


PLATE 8

*Conditions of Tests.*

Speed: 1. 225 R. P. M.

2. 175 R. P. M.

Surface: 1. 3 to the inch straight cut and 12 to the inch spiral cut.

2. 6 to the inch spiral cut.

Pockets used: 3 at a time.

Process: Hot Grinding.

## YIELD PER CORD AND QUALITY OF PULP

The condition of the surface of stone has very little effect upon the yield per cord of wood. It is true that with extremely sharp stones there are more screenings formed, and possibly more wood fiber finds its way into the white water, but within reasonable limits of sharpness the yield is very slightly influenced.

On Plate 3 are shown two photomicrographs of pulps obtained on stones of different degrees of sharpness. In one case a power consumption of 84.5 horsepower per ton was required, while in the other only 64 horsepower was used. It will be noted that the better quality of pulp is produced at higher power consumption and lower degree of sharpness of stone.

## PRESSURE ON GRINDER CYLINDERS

The pressure at which the wood is forced upon the revolving grindstone varies greatly with the diameter and length of the material for any given cylinder pressure. There is liable to be considerable binding of the wood in the grinder pockets also, and this, too, results in a variation of the pressure on the stone. It

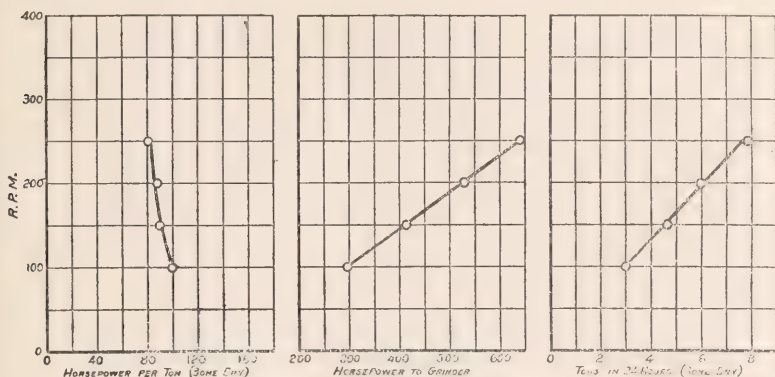


PLATE 9

*Conditions of Tests.*

Pressure: No. 60 on 14" cylinder.

Surface: 3 to the inch straight cut and 12 to the inch spiral.

Pockets used: 3 at a time.

Process: Hot Grinding.

is reasonable to suppose, though, that the variations due to these factors are fairly constant for any cylinder pressure and consequently do not effect the deductions regarding the relative influence of different cylinder press res upon factors of economic production.

*Horsepower per ton. Horsepower to the grinder.  
Production in 24 hours.*

Plate 4 shows graphically the relations between the pressure in the grinder cylinders and the horsepower per ton power to the grinder, and production in 24 hours. The three curves shown were obtained on surfaces of different degrees of sharpness. It will be noted that on the stone of greatest sharpness there is a very slight decrease in the power consumption per ton with increasing pressure and that on the duller stone there is a marked decrease of power consumption as the pressure is raised. It will also be noted that the curves converge, thus indicating that it is impossible to produce pulp at powers lower than a certain value (approximately 50 horsepower) regardless of the pressure used in grinding or the surface of stone.

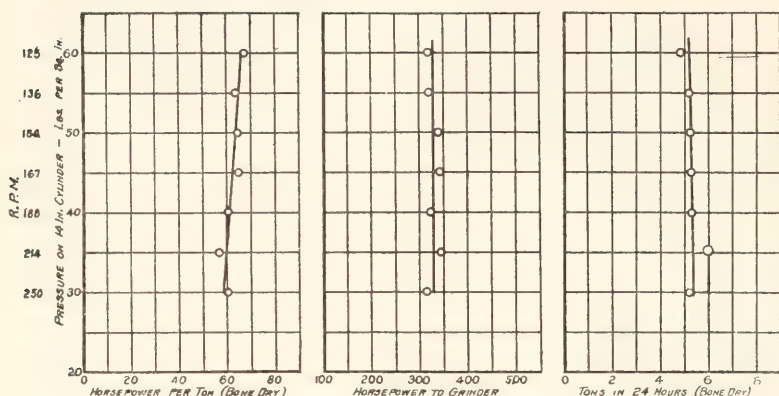


PLATE 10

*Conditions of Tests.*

Surface: 3 to the inch straight cut and 12 to the inch spiral cut.

Pockets used: 3 at a time.

Process: Hot Grinding.

The power to the grinder varies directly with the pressure on the cylinders as also does the production in 24 hours.

Plate 5 shows the relations between the same factors as on Plate 4. Here, however, only two pockets in the grinder were used and the pressure was raised to a much higher value. The decrease in power consumption with increasing pressure will be noted.

As in Plate 4, the power to the grinder and production in 24 hours vary directly with the pressure on the grinder cylinder.

On Plate 6 is shown the relation between the number of pockets used and the horsepower consumption per ton of pulp. In this test the power to the grinder and the speed were maintained constant, the power being utilized by raising or lowering the cylinder pressure, depending upon the number of pockets used. It will be noted that when using one pocket corresponding to the pressure of 120 pounds per square inch the horsepower consumption per ton was 58, while when all of the power was used on three pockets, the pressure of  $36\frac{1}{2}$  pounds was maintained on each grinder cylinder, and the power consumption per ton was approximately 89 horsepower. This is only another way of demonstrating that the power consumption per ton of pulp in 24 hours is much lower at high pressure than at low pressure.



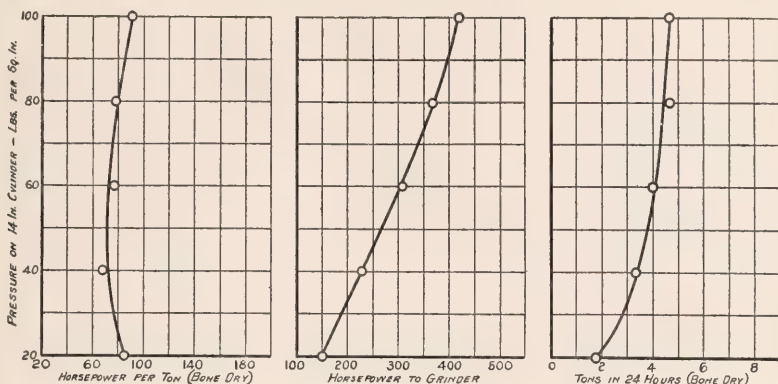


PLATE 11

*Conditions of Tests.*

Speed: 225 R. P. M.

Surface: 3 to the inch straight cut and 12 to the inch spiral.

Pockets used: 2 at a time.

Process: Hot Grinding.

Wood Treatment: Steamed 6 hours at 60 pounds pressure before grinding.

## YIELD PER CORD AND QUALITY OF PULP

On Plate 7, Fig. 2, is shown graphically the relation between yield per 100 cubic feet of solid wood and the pressure on the grinder cylinder. It is evident that with increasing pressure the yield of pulp increases. It is true that the amount of screenings also increases, but the gain at higher pressures is due to there being less pulp in the white water.

The effect of pressure on the quality of the pulp, as indicated by the strength of the paper, is shown on Plate 8. Here the strength factor, the bursting strength per square inch divided by the weight per ream, decreases with increasing pressure. The decrease in the strength of paper with the power consumed in making a ton of pulp is also shown.

## PERIPHERAL SPEED OF STONE

The peripheral speed of stone is a factor which commercially is in most cases only slightly considered, and rightly. When the pressure on a pocket is removed, unless a governor controls the

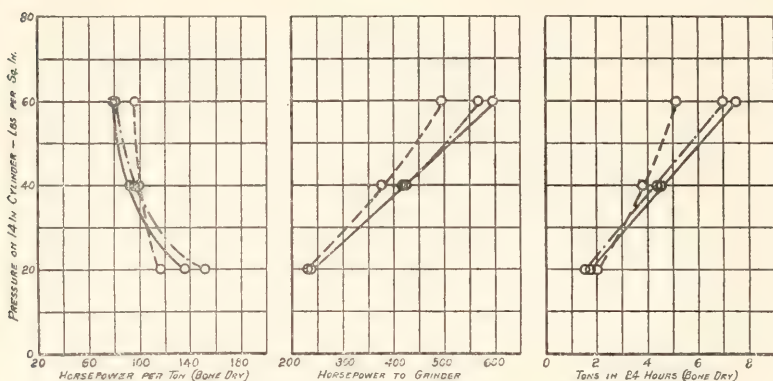


PLATE 12

*Conditions of Tests.*

Speed: 225 R. P. M.

Surface: 3 to the inch straight cut and 12 to the inch spiral.

Kinds of Woods: Full line. Green Spruce.

Dash and dot. Seasoned Spruce.

Dashed line. Steamed Spruce.

Treatment of Wood: Steamed 4 hours at 60 pounds pressure.

Pockets used: 3 at a time.

Process: Hot Grinding.

speed, it will increase greatly. The influence of this increased speed, however, is generally more beneficial than otherwise, since it is a means of increasing the production of pulp while only two pockets are in operation.

*Horsepower per ton. Horsepower to the grinder.*

*Production in 24 hours.*

Plate 9 shows the relation between revolutions per minute of the pulpstone and the horsepower per ton, horsepower to the grinder, and tons in 24 hours. It will be noted that with increasing speed the power consumption per ton gradually becomes less, while the power to the grinder and production in 24 hours vary directly with the speed of the stone.

On Plate 10 are shown the relations between the speed and cylinder pressure and the horsepower consumption per ton,

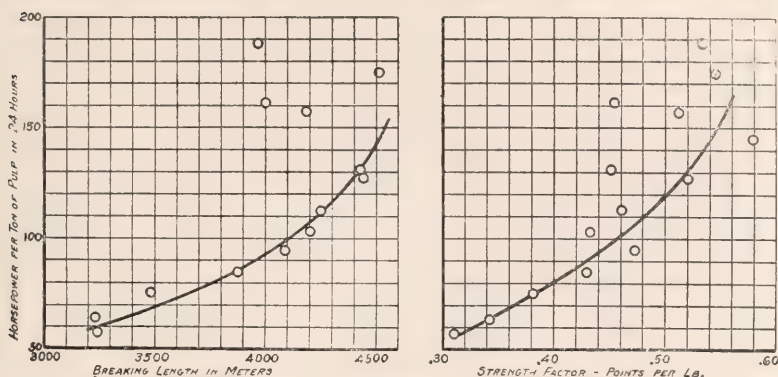


PLATE 13

VARIATION OF STRENGTH OF PAPER WITH POWER USED IN THE MANUFACTURE  
OF THE MECHANICAL PULP

Points are averages of 60 values

power to the grinder, and production in 24 hours. In these tests the power to the grinder was maintained as nearly constant as possible, the pressure and speed being adjusted to different values so as to utilize the power in each case. It will be noted that with constant power to the grinder the production in 24 hours is constant regardless of whether or not the pulp is produced at high speed and low pressure or low speed and high pressure. It will also be noted that the power consumption per ton, while increasing slightly with low speed and high pressure, is practically constant.

YIELD PER CORD AND QUALITY OF PULP

The yield per cord and quality of the pulp are only influenced slightly by the speed. The yield appears to be somewhat higher with high speed production. The difference, though, over low speed production is small. The quality, as determined by strength tests of paper made from the pulps, is not influenced in a regular manner as it is by the pressure of grinding.

THE MOISTURE CONTENT, WEIGHT PER CUBIC FOOT, AND  
CONDITION OF THE WOOD

The question of the influence of moisture content and condition of the wood is a very important one. Wood for pulp purposes is

almost invariably allowed to season for a long period before using. As a result it becomes dark colored and will not yield the long fine fibers which can be obtained from green wood. The treatment of wood prior to grinding, by steaming, boiling or some other like process, is important also because by this manner of treatment better fibers can be obtained from wood which, when ground in the natural state, yields pulps which are very short fibered. In this way, too, pitchy woods are made usable by the mechanical process.

*Horsepower per ton. Power to the Grinder.  
Production in 24 hours.*

On Plate 11 is shown graphically the relations between the pressure of grinding and the power consumption per ton, power to the grinder, and production in 24 hours when the wood used had been steamed prior to grinding for 6 hours at a steam pressure of 60 pounds per square inch. It will be noted that the power consumption per ton is a fairly constant quantity and that there is a decided contrast between values of power consumption, power to the grinder, and production in 24 hours obtained on steamed wood and values obtained on seasoned untreated wood as given on Plate 6.

The power to the grinder under like conditions of speed and pressure is much less when steamed wood is used than when the wood is unsteamed, and this is also true of the production of pulp in 24 hours.

On Plate 12 is shown the relation between the pressure on the grinder cylinders and horsepower consumption per ton, power to the grinder, and production in 24 hours. These tests were conducted using green, seasoned, and steamed wood. It will be noted that the power consumption generally is lower for seasoned wood than for steamed wood, and still lower for green wood than for either seasoned or steamed wood.

The power to the grinder required for either seasoned or green wood under like conditions of speed or pressure is essentially the same. The power is less, however, when steamed wood is used, this undoubtedly being due to the lubricating action of the steamed material.



It will be noted that the production of pulp from green wood is greater than from seasoned wood; also that the production of steamed wood is less than for either of the other two materials.

#### YIELD PER CORD AND QUALITY OF PULP

The yield per cord is much less when the wood is given a steaming treatment than when it is ground in the natural state. However, practically the same amounts of pulp can be obtained from green or seasoned wood when produced under the same conditions of grinder operation. The thing which most influences the yield is the bone-dry weight of the wood. On Plate 7, Fig. 1, is shown graphically the relation between these two factors. It will be noted that the yield of pulp is directly proportional to the bone-dry weight of the wood; in this case different kinds of woods were used in the tests.

The quality of the pulp can, of course, only be measured by its suitability for use in different paper. The pulp produced from steamed wood is dark in color but very strong. That produced from very dry wood is invariably of shorter fiber and darker color than that obtained from green wood under like conditions. However, the green wood contains more pitch and this may cause trouble in the operation of the paper machines.

#### TEMPERATURE OF GRINDING

The temperature of grinding has almost no influence upon the power consumption per ton, power to the grinder, or the production in 24 hours. Likewise it does not seem to influence the yield from a cord of wood. The quality, in so far as strength and toughness are concerned, is influenced, pulp of better quality being obtained under conditions of hot grinding. In this case, as in others, however, the measure of quality is the adaptability of the pulp to use in the desired sheet of paper and it is unquestionably true that for certain purposes pulp produced by the cold grinding process is more desirable than that of the hot process.

#### INFLUENCE OF POWER EXPENDED IN PULP MANUFACTURE ON THE STRENGTH OF PAPER MADE THEREFROM

There is shown graphically on Plate 13 the relation between the power consumption per ton of mechanical pulp in 24 hours



and the strength factor and breaking length of paper made from the pulp. The results here plotted are the averages obtained under many different conditions of surface of stone, pressure, speed, temperature, etc. It is evident from this curve that in order to make strong paper it is necessary to consume considerable power in the manufacture of the mechanical pulp. This, of course, does not take into consideration the possibilities of refining processes. The strength factors shown, even for pulps of low power consumption, are equal to or greater than values obtained for newspaper in commercial practice. This may be due, however, to the fact that a small paper machine and much care were used in the manufacture of the paper; also to the fact that the strength tests were made on uncalendered paper.

#### CONCLUSIONS

1. The power to the grinder increases directly with the speed and pressure, and inversely with the degree of sharpness of the stone. There is also a very slight increase with the temperature. Under like conditions of all other factors the power to the grinder is less for steamed wood than for green or seasoned wood untreated.

2. The production of pulp in 24 hours varies directly with the pressure, speed, and the degree of sharpness of the surface of stone. Less pulp is obtained in 24 hours from seasoned wood than from green, and still less from steamed wood, all other conditions being the same.

3. The horsepower consumption per ton on untreated wood increases as the pressure decreases according to a fairly definite law; it is lower on sharp stones than on dull and it increases as the speed decreases in much the same manner as is the case with pressure. There is, however, not as much difference between the power consumption per ton at low speed and at high speed as there is between power consumption at low pressure and high pressure. The temperature has very little influence on power consumption; it is slightly lower at high temperatures. The power consumption per ton is higher for seasoned wood than for green wood, and still higher for steamed wood than for either seasoned or green wood ground under the same conditions. Conifers require more power per ton of pulp produced than hard woods.

4. The yield of pulp per cord is greater at high pressure than at low, and this is also true of screening. There is, however, not as much fine material lost in white water when high pressure is used. The surface of the stone does not greatly influence the yield per cord. The yield is slightly higher at high speed than at low and it is directly proportional to the bone-dry weight per cubic foot of wood.

5. The quality varies greatly with the surface of the stone, less greatly with the pressure, and least with the speed. The weight per cubic foot and character of wood influence it to a marked extent, especially the latter. The temperature has a marked influence, pulp of higher quality being obtained at higher temperature. Pulp of better color can be obtained from green wood than from seasoned, and stronger pulp can be obtained by steaming the wood prior to grinding. The quality of paper produced under exactly the same conditions but made of pulps produced at different grinder pressures varies directly with the grinder pressure and the horsepower consumption per ton of pulp. Pulp of highest quality can only be produced from a definite kind of wood by the expenditure of a large amount of power.



### *Abstract*

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## ESTIMATION OF CELLULOSE. CELLULOSE METHODS VERSUS CRUDE FIBRE (ROHFASER) METHODS

BY C. F. CROSS AND E. J. BEVAN

*London W. C., England*

In a series of articles published in the *Zeitschr. Farb. Ind.* vols. 10-11 (1911-1912) are set forth the results of elaborate experimental investigations by the authors, J. König and Fr. Hühn, with their general conclusions as to methods of isolating and estimating cellulose.

They advocate "Rohfaser" or "Crude Fibre" methods followed by specific oxidising treatments for removal of lignone residues, and dismiss the "cellulose" methods, notably those more generally adopted—viz., chlorination (Cl. Aq, Cross & Bevan), Bromination (Br Aq, H. Müller), since they yield according to the authors, heterogeneous mixtures of true cellulose ["wahre cellulose"] pentosanes, furfuroids, and hemi-hexoasanes.

It has been deemed opportune to submit this communication to critical analysis, as it seeks to assail the foundations of cellulose technology as generally accepted, and to reverse the judgment of the sub-committee on analyses which reported to the Seventh International Congress (London).

It is now shown that the "residues" which the authors obtain either by their process, which is selected in the first place, or by that of Tollens and Dmochowski, also a "Rohfaser" method, proposed in the second place, are advanced products of decomposition and disintegration.

They have no claim to be regarded as celluloses, and the confusion of such products with "cellulose" not only obscures the natural relationships of the celluloses, but leads the authors into a number of mistakes both of experimental numbers, as of interpretations of numerical results correct in themselves.

The most prominent of these are pointed out and discussed.

A fundamental error is to regard, as they do, the chlorination process as a process of oxidation.

On this point some special experimental work is now recorded in which the two processes of attack of lignone residues, *viz.*, by Cl Aq and by Br Aq are contrasted.

In the latter case the action of the halogen is in effect complicated by oxidations, which under severe conditions of action are considerable in relation to the degree of bromination.

In the case of chlorine gas, the minimum of secondary action (oxidation) is further reduced under special conditions of reaction, *viz.*, absence of light and low temperature.

The authors have no hesitation in anticipating the judgment of competent critics of this attempt to substitute the present methods of cellulose estimations, by methods based on the "Rohfaser" of the agronomic chemists.

The former are based on the natural perspective of the celluloses, as (1) products of plant life, (2) the basis of our most important manufactures and (3) chemical individuals defined by laboratory methods both statistical and constitutional.

The "Rohfaser" residues are products of degradation by treatments more or less arbitrary, because relatively non-selective in their actions, which are moreover ill-defined through the complex and unascertained relation of products to the mother substances.

Further, the particular process commended by the authors involves long, drawn-out manipulations out of all relation to the exigencies of technical investigations.

Both on practical as well as scientific grounds, therefore, the authors fail to justify their attack upon a position based upon "natural science" and the accumulated experiences of a generation of scientific and industrial technologists.



## ANTISEPTIC TESTS OF WOOD PRESERVING OILS

BY A. L. DEAN AND C. R. DOWNS

*Yale University, Sheffield Scientific School, New Haven, Conn.*

The materials commonly employed for impregnating wood for the purpose of preventing its decay fall readily into two classes,—soluble salts and hydrocarbon oils. The most widely used member of the first group is zinc chloride, and of the second, coal tar creosote. Ever since the introduction of this last named material by Bethell in 1838 it has been employed in constantly increasing amounts, and today creosoting—properly performed—is regarded as the most effective method of timber preservation.

In recent years the large demand for coal tar creosote and the rather high cost of the treatment with the amounts considered necessary, have led to the use, openly and otherwise, of other materials. Thus the heavy asphaltic petroleum oils have been tried to some extent, notably in the treatments by the Santa Fe railroad where sufficient of the oil has been injected to render the wood well-nigh waterproof. The oil distilled from the tar resulting from the manufacture of carburetted water gas has been used to a considerable extent, but since its value was uncertain it has been regarded as an adulterant or substitute for the oils distilled from coal tar. Water gas tar shows many points of similarity to coal tar, and the creosote oil distilled from it is very like that distilled from coal tar, although it contains neither the phenols nor the nitrogenous bases characteristic of the latter. Inasmuch as large quantities of water gas tar are produced at the gas works in the United States, and the creosote distilled from it might readily be had in substantial amounts, it is important to arrive at a sound estimate of its value as a timber preservative.

The qualities commonly desired in a wood preserving oil are freedom from loss by volatilization, solution or chemical change, and a marked toxicity to wood rotting fungi and the animals which destroy timber.

In volatility, solubility and chemical inertness water gas tar

creosote compares favorably with the oils from coal tar; the relative antiseptic powers of the two classes of oils is less readily determined. The present communication outlines the results of a laboratory study of the antiseptic powers of oils prepared from coal tar and water gas tar, and is designed to assist in arriving at a proper estimate of the place that water gas tar oils should occupy in timber preservation.

The value of water gas tar creosote as a wood preservative has been the subject of some controversy, but as yet the amount of reliable data has not been large. Practical tests on a commercial scale giving the results of the test of time under service conditions have not been carried out. Where the material has been used it has usually been employed in mixture with coal tar creosote, sometimes without the consumer's knowledge. The result has been that in the absence of reliable information consumers have preferred to rely on coal tar creosote of the value of which they were certain.

Alleman<sup>1</sup> has studied the character of the oils remaining in timbers which, after being treated with coal tar oils, have been many years in service. The results show that the low boiling oils present in creosote disappear after a number of years of service, and the tar acids or phenols are no longer present. There has been in recent years a growing tendency to regard these high boiling hydrocarbon oils such as Alleman found remaining in his well preserved timbers as the most valuable constituents of creosote oils.

During 1911 J. M. Weiss<sup>2</sup> presented two papers to the New York Section of the Society of Chemical Industry dealing with the antiseptic value of the oils and tars used in timber preservation. These papers showed the relative antiseptic value of coal tar oils and water gas tar oils under the conditions of Weiss' experiments, as well as furnishing some information on the relative values of the different tar oil constituents. These papers furnish the most important experimental evidence of the antiseptic powers of the

<sup>1</sup>Gellert Alleman. Circular 98, Forest Service of the U. S. Department of Agriculture, May, 1907.

<sup>2</sup>J. M. Weiss. *Journal of the Society of Chemical Industry*, Feb. 28, 1911, p. 190, and Dec. 15, 1911, p. 1348.

different oils. The work of Weiss showed that coal tar creosote was many times as toxic to the organisms used in his experiments as the water gas product, and that the lower boiling coal tar oils were distinctly more antiseptic than the heavy high boiling ones.

Two criticisms may be made of the methods employed by Weiss. The first, and less important, being that the fungi used by him to test the antiseptic powers of the materials experimented on by him were not wood destroying fungi and their powers of resistance to various agents might not be the same. A much more serious objection to his results depends upon the method employed in preparing the media containing the oils to be tested. These are for the most part insoluble in water, and being heavy, sink rapidly to the bottom of the containing dishes, so that a uniform distribution of the oil is not effected, and the cells of the fungi may not come in contact with it. It is apparent that oils containing water soluble constituents would partially dissolve and prove more antiseptic than the more insoluble oils. It might readily be that the relatively greater antiseptic power of the lighter coal tar oils was partly due to solubility of the phenols present in them, the toxic power of which is well known. It would seem that a much fairer idea of the antiseptic power of the oils tested could be gained if they were uniformly distributed throughout the culture medium so that the fungus must come in contact with them.

The organism used in the experiments to be described was *Polystictus versicolor* obtained in pure culture from wood decaying through the action of this fungus and tearing masses of its sporophores on the surface. Numerous cultures were kept in the laboratory on small blocks of sterilized *Liriodendron* wood on which it grew readily, and which it reduced to about the specific gravity and strength of pith in the course of a few months. There was no doubt of the purity of the cultures nor of the powerful attack of the fungus on the wood. This species was used because of the readiness with which it may be isolated in pure cultures which grow vigorously under laboratory conditions, and also because it is one of the most important enemies of structural timber in the United States. Von Schrenck<sup>1</sup> says of this species:

<sup>1</sup>Von Schrenck. Bulletin 149, Bureau of Plant Industry of the U. S. Department of Agriculture, p. 53.

"Of all the fungi which grow upon the deciduous species of woods after they are cut from the tree, the most widely distributed and in many respects the most destructive is *Polystictus versicolor*. . . . On account of its wide geographical range and its ability to grow on and destroy so many different kinds of wood it should be regarded as the most serious of all the wood-rotting fungi which attack the dead wood of broadleaf trees. It is the fungus which destroys probably 75% or more of the broadleaf timber used for tie purposes."

Inoculations into the media to be tested could not be conveniently made from cultures growing on wood and transfers were therefore made to prepared agar from which the fungus could be readily cut and small masses of the mycelium transferred by the use of a small piece of platinum foil set in a glass handle.

The culture media were prepared in the following manner. Ordinary white beans (*Phaseolus vulgaris*) were germinated in a dark place until several inches high. The seedlings were then ground up in a meat chopper and a boiling water extract of them made. Due to the chemical changes characteristic of the process of germination some of the starch of the beans is hydrolysed to dextrins and sugar, and much of the nitrogen present as the proteins of the seeds appears as soluble cleavage products in the seedlings. One-half of one per cent of cane sugar and a like quantity of asparagin were added to the germinated bean extract to supply further nourishment. This medium was then stiffened by the addition of 1.5% of agar agar, and 10 cc. portions of it pipetted hot into 22 mm. test tubes, plugged with cotton and sterilized.

A five-gram portion of each of the creosote oils to be tested was weighed out into a mortar containing an equal weight of powdered gum arabic and the two rubbed well together. Water was then added a little at a time with constant grinding, yielding an emulsion containing as the emulsifying agent a carbohydrate material similar to the agar agar of the medium. The emulsion was diluted with water to 100 cc., making a 5% emulsion which would not separate even after several months of standing.

Portions of these five per cent emulsions were measured into the 10 cc. portions of the sterilized agar medium with a pipette



graduated to hundredths of a cubic centimeter. As a rule three test tubes of each strength were prepared in order to check the results. The agar was then melted and the tubes well shaken in order thoroughly to mix the emulsion with the medium, and then quickly cooled under cold water in a slanting position. In this way the oil was uniformly distributed throughout the medium in the form of finely divided globules and held permanently in position by the solidification of the agar.

In the first series of tests the oils used were a very good grade of commercial coal tar creosote, a water gas tar creosote made in the laboratory by taking the fraction distilled from 170° to 340°C. from a sample of water gas tar of known origin, and a sample of pressed anthracene oil. The results of the fractional distillation of the two first samples are given in the table below.

| Temperature | Coal tar creosote | Water gas tar creosote |
|-------------|-------------------|------------------------|
| 170°C.      | 0.2%              | 5.5%                   |
| 170° 205°   | 6.3%              | 4.5%                   |
| 205° 240°   | 30.7%             | 35.5%                  |
| 240° 300°   | 21.3%             | 32.5%                  |
| 300° 320°   | 9.1%              | 6.0%                   |
| 320° 340°   | 13.5%             |                        |

The coal tar oil contained 8% of tar acids. The anthracene oil was a commercial product, 50% of which distilled between 250° and 350°C. The solids had been pressed out, leaving it liquid at room temperatures.

The strengths of coal tar creosote tested varied by .05% increments from .05% to .35%, and of the other two oils from .05% to .75%.

The results of this preliminary series indicated an inhibition point for the fungus with .25% of coal tar creosote, .40%-.45% of the water gas tar creosote, and over .75% for the pressed anthracene oil. In the case of the last named material the growth became progressively weaker, but was not entirely inhibited at the highest concentration tried.

One serious difficulty developed in the tests. In transferring the fungus mycelium to the test tubes it was necessary to cut out a small piece of the agar of the stock culture and it was almost



impossible to tell whether the fungus was growing slightly on the creosoted agar or whether all the growth was derived from the small piece of transferred medium. This led to some uncertainty as to the precise point at which growth was inhibited. In the second series, this was remedied by cutting out a small piece of the medium to be inoculated with a sterile platinum foil, laying the cut out piece over to one side, placing the transferred mycelium and agar from the stock culture in the cavity, and then replacing the piece of creosoted medium on top of the transferred material. In this way the mycelium used for inoculation was buried within the mass of material to be tested and if it grew up through it and vegetated at the surface there could be no question that the antiseptic was insufficient to prevent the growth of the fungus. The control cultures were made in the same manner.

The too rapid drying out of the cultures noticed in the first series was prevented in the second by placing them in a large glass walled case with a water saturated atmosphere.

Since the fungus used in the first series might have had its vitality somewhat impaired by being kept so long in artificial cultures, new samples of wood decaying through the action of the organism were found and fresh pure cultures prepared and used for inoculating the second series of tests. The following oils were tested.

A. Coal tar creosote No. 1.

B. Coal tar creosote No. 2, prepared in the laboratory by taking the fraction distilling from  $200^{\circ}$  to  $350^{\circ}\text{C.}$ , from a sample of coal tar; since there was a considerable separation of naphthalene in this sample on cooling to room temperature, which rendered it impossible to make a satisfactory emulsion, the solids were filtered off.

C. Water gas tar creosote No. 1.

D. Water gas tar creosote No. 2, prepared in the laboratory by taking the fraction distilling from water gas tar between  $200^{\circ}$  and  $350^{\circ}\text{C.}$ , yielding a sample somewhat heavier than the No. 1 and comparable in boiling range with coal tar creosote No. 2.

E. The same sample of pressed anthracene oil used in the first series.

F. Coal tar creosote No. 1, washed with alkali until free from tar acids and then washed with water.

G. A portion of F. with the tar bases removed by treatment with sulphuric acid, and washed with water.

An attempt was made to make emulsions with anthracene and naphthalene for antiseptic tests in the manner described above for the oils, but was found impossible to make satisfactory emulsions. The attempted stock emulsions of these materials containing about 5% of the hydrocarbons stood for some time in the laboratory and it was noted that a mould growth appeared on the surface. The naphthalene and anthracene had settled to the bottom. This observation would tend to support the statement made by Weiss that these materials were not antiseptic up to 10%. This conclusion seems not to be wholly justified, however, because the mould was not in contact with the hydrocarbons.

The results of the tests in the second series were as follows:

| Sample                                       | Inhibition Point |
|--|------------------|
| A. Coal tar creosote No. 1                   | Below .4%        |
| B. Coal tar creosote No. 2                   | .4%              |
| C. Water gas tar creosote No. 1              | .4%              |
| D. Water gas tar creosote No. 2              | .35%             |
| E. Pressed anthracene oil                    | Above .85%       |
| F. Sample A. minus the phenols               | .30%             |
| G. Sample A. minus the phenols and tar bases | Above .6%        |

In the case of sample E. there was a gradual weakening of the growth from .2% to .85% which was the highest concentration tried, and a similar state of affairs developed in the tests of sample G., the highest strength of which was .6%. Of the two the cultures with sample E. were slightly the more vigorous.

From these results it is evident that coal tar creosote is a stronger antiseptic than water gas tar creosote, and that water gas tar creosote is distinctly more effective than the liquid oils of the anthracene fraction of coal tar. The greater value of the coal tar oil appears to depend upon the presence of the tar acids and especially upon the tar bases. It is interesting to note that the water gas tar creosote was almost identical in antiseptic power with the coal tar oil with its tar acids removed.

The work of Alleman cited indicated that the oils remaining in wood treated with coal tar creosote are almost free from

tar acids after a few years of service, and that under conditions allowing evaporation the lighter hydrocarbons are nearly all lost. Loss of antiseptic power from the disappearance of the tar acids cannot take place with water gas tar oils, since they are free from phenols in the beginning.

Since the amount of creosote injected into wood is commonly 10 pounds per cubic foot or more, it would appear that the difference in antiseptic value between coal tar oils and water gas tar oils is not of great significance, especially in view of the probable disappearance of the tar acids from the wood treated with coal tar creosote.

On the basis of such data as we have it seems justifiable to conclude that the oils distilled from water gas tar have a distinct value as wood preservatives, and that there is no reason why they should not be purchased and used under their own names with no attempt to masquerade as coal tar products.

# THE PRESENCE OF MALTOSE IN ACID HYDROLYSED STARCH PRODUCTS

BY GEO. DEFREN

*Newton, Mass.*

Earlier discussions about the hydrolysis of starch by acids assumed the presence of maltose as one of the intermediate products between soluble starch and dextrose.

Maltose is formed usually by the action of diastase on starch. This maltose can be easily hydrolysed to dextrose by acids; and, as dextrose was the final normal product of acid hydrolysis of starch, it was natural to assume that maltose must have been an intermediate product.

The fact that the curve representing the cupric reducing powers at various rotations is an arc of a circle, and, at its centre, lies considerably above the chord limiting the beginning and the end of the hydrolysis as produced by acids, indicates that some other influence, in addition to that of dextrose, is a factor in producing the curve, and this has been attributed to maltose.

Effort<sup>1</sup> had been made to separate the maltose by eliminating the dextrin by precipitation with alcohol. This was a difficult undertaking, as dextrose was also somewhat soluble in alcohol, and the phenyl-osazones melt only one degree C. apart. Crystals corresponding to phenyl-maltose-azone were obtained, but free maltose had not been isolated.

It occurred to the author to try a different method. As dextrose had to be eliminated—as well as any dextrin present—it was determined to ferment this hexose from the mixture. Advantage was taken of the fact that *sac. apiculatus* ferments dextrose, but not maltose—or, at any rate, the latter less actively.

As acid hydrolysed starch products have varying percentages of carbohydrates at different optical rotations, it would be advantageous to select a mixture which would have maximum maltose present. This should be theoretically between  $[\alpha]_D$

<sup>1</sup>Jour. Am. Chem. Soc. 25, 1015.

150° and  $[\alpha]_D$  110°. A high rotating glucose of  $[\alpha]_D$  150° would have little dextrose to ferment, but much dextrin to eliminate by precipitation, while a mixture at  $[\alpha]$  110° would have much more dextrose, but only one-third as much dextrin.

A product of  $[\alpha]_D$  144° was first taken, yeast water, and ammonium phosphate added, then impregnated with *sac. apiculatus* and fermented. The alcohol was removed by distillation, and the remainder again subjected to fermentation.

The residue was concentrated, poured into a large volume of boiling 90% alcohol, and the precipitate allowed to settle. The supernatant liquid was filtered, concentrated to a thick syrup, and its contents allowed to crystallize. The dark, thick crust was redissolved in boiling water, decolorized with bone black, and again crystallized. The final product was a white crystalline powder which showed all of the physical properties—optical rotation, copper reduction, and formation of osazone—characteristic of maltose obtained heretofore only by the action of diastase on starch.

Fermentation experiments were also made with an acid converted starch product of  $[\alpha]_D$  110°. This gave the maltose more easily than did the glucose of 144°, probably owing to the fact that there was much less dextrin to eliminate by alcohol precipitation.

This isolation of pure maltose thus puts an end to the oft repeated contention that dextrose only results from the action of acids on starch.



# THE HYDROLYSIS OF STARCH BY ACIDS, WITH SOME ADDITIONAL RESULTS ON THE SPEED OF HYDROLYSIS

BY GEO. DEFREN  
*Newton, Mass.*

Commercial analyses of malt worts and similar products of the action of diastase on starch are based on the assumption that but two simple compounds are formed—maltose and dextrin. In the case of glucose-starch syrup and starch sugars, which are the product of acid hydrolysis, it is known that the reaction proceeds further, and that dextros (d-glucose) is formed.

Investigation has shown that all of these compounds are present in the solutions produced by acid hydrolysis of starch, and that consequently the reactions forming them must have gone on together. Evidently there are quite a number of intermediate products—molecular complexes—of dextrin and maltose<sup>1</sup>, which have different optical and copper-reducing powers, and have different coloring properties with iodine.

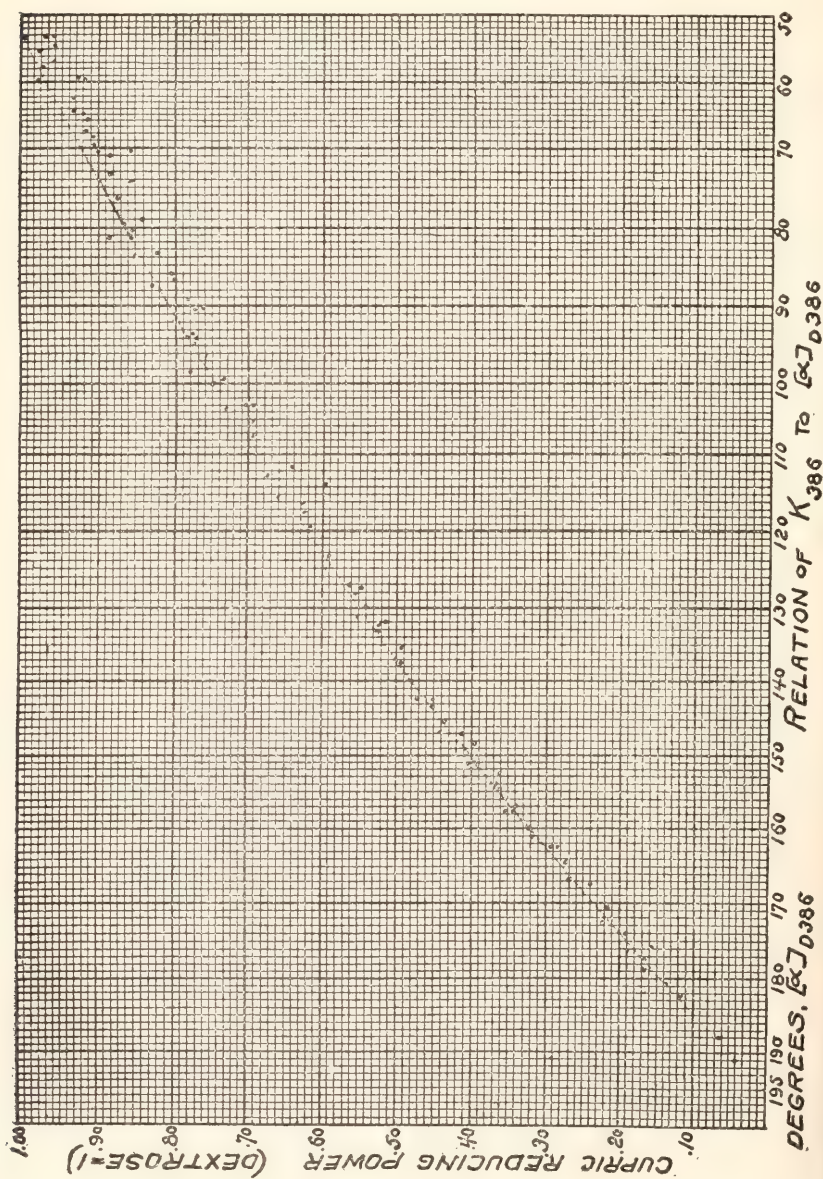
It has been shown<sup>2</sup> that at any stage of the conversion of starch by diastase, the total product in its optical properties, and relation to Fehling's Solution, behaved exactly as if made up of two components only—dextrin and maltose—so that it was possible by taking the rotatory power, to calculate at once the reducing power, if the weight of the total carbohydrates were known. This law indicated that, however complicated the bodies isolated, they could be considered as existing in solution as two simple substances, and did much to establish the principles of the usual commercial analyses of worts and similar products.

The methods of analysis of glucose syrups and starch sugars implied the assumption of a similar law, such has been shown to be the case.<sup>3</sup> A large number of conversions of starch were made under varying conditions of temperature and concentration of

<sup>1</sup>Ber. d. Chem. Ges. 28. 1522–1531.

<sup>2</sup>Am. Chem. (Liebig) 231, 131.

<sup>3</sup>Jour. Am. Chem. Soc. XVIII. No. 10.



different acids, but the results were invariably the same. In other words, the values obtained pointed to the remarkable fact that the cupric reducing power of the total product bears a constant relation to the specific rotatory power, even when the starch has been hydrolyzed by acid under widely varying conditions. Hence, given the one, the other could be calculated.

The relations between the optical rotations and the cupric reducing powers are shown graphically in Plate A.

The upper part of the curve is not so well defined, the results showing more discrepancy at the high conversion stages. This may be due to some decomposition, or so-called "reversion products."<sup>1</sup> That the solutions begin to color considerably beyond 90, is, moreover a strong indication of such decomposition.

By taking the optical properties  $[\alpha]$  and the reducing powers ( $k$ ) of dextrin ( $d$ ), maltose ( $m$ ), and dextrose ( $g$ ), in acid hydrolyzed starch mixtures, we get several equations. The results are given graphically in Plate B.

<sup>1</sup>Ber. d. Chem. Ges. 231, 2101.

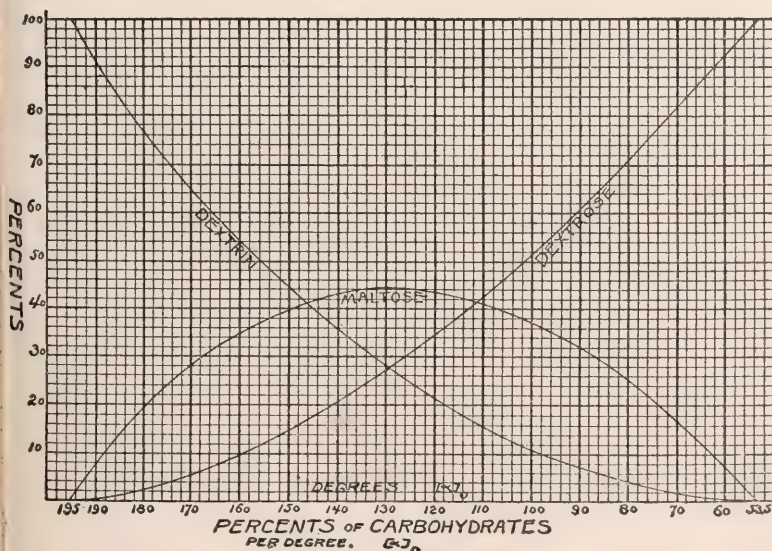


PLATE B



Examining these curves, we see that dextrin, starting from a maximum of 100%, gradually falls to "zero" near the rotation corresponding to that of dextrose. The percentage of maltose gradually rises, reaches a maximum of 46.2% at about  $[\alpha]_D 129^\circ$ , corresponding to the usual state of commercial glucose-starch syrup—and then falls, disappearing at  $53.5^\circ$ . The dextrose, on the contrary, steadily mounts to 100%.

These plots do not take into consideration the presence of any decomposition products which are evidently present in slightly increasing amount between the rotations of  $[\alpha]_D 90^\circ$  and  $[\alpha]_D 53.5^\circ$ , to which reference has already been made. Some investigations have already been undertaken concerning these decomposition products, but as yet with no tangible results.

To summarize the above results: We find that starch is first liquefied by boiling water, forming the so-called "starch paste," or amylo-dextrin, which colors iodine deep blue. In the presence of any acid which dissociates in water solution, this amylo dextrin is hydrolyzed, taking water into the molecule, and producing complexes of dextrin, and maltose, and called, collectively, "malto-dextrins." These have varying optical and copper reducing powers and are effected differently by iodine, those of higher molecular weight giving blue or violet colorations and changing gradually into dark red or brown, then going over into yellow, and finally becoming colorless when the rotation falls below  $[\alpha]_D 140^\circ$ . Further addition of water to the molecule results in the formation of free maltose, which is itself then hydrolyzed into dextrose by the addition of another molecule of water. Dextrose is, then, the final normal product of the hydrolysis of starch by acids.

#### THE SPEED OF HYDROLYSIS OF STARCH BY ACIDS

The development of physical chemistry in recent years has shown that the hydrolysis of substances in solution by acids is due to the action of the dissociated hydrogen ions of these acids. Assuming that the amount of acid and the temperature remained constant, the rate of inversion at any specified moment is proportional to the amount of unchanged substance present at that moment. That has been proved to be the case with cane sugar, salicin, and many other substances.

The observations noted above suggested the possibility that in the hydrolysis of starch the acids should show the same proportionate speed of reaction. This is an especially interesting problem because the starch molecule is exceedingly complicated, the molecular weight being undoubtedly very high. Some work which we have done has shown results above 33,000.

Starch hydrolysis, however, must be considered as somewhat different from that of cane-sugar or salicin. While these latter are easily soluble in cold water, starch is totally insoluble at ordinary room temperature. On the other hand, amylo-dextrin, the product of decomposition of starch by boiling water, is somewhat soluble in cold water, its solubility increasing with rising temperature.

As by the customary procedure in determining speed of hydrolysis, it would be necessary to ascertain the exact moment when all the starch has been converted into soluble form, a point not conveniently determined, a method of measurement based on the following principles has been adopted.

The conversion products of starch, with the possible exception of those of very high rotatory power, are easily soluble in water, and can be looked upon as mixtures of dextrin, maltose, and dextrose. The starch first changes to amylo-dextrin; this then goes over into maltose and finally dextrose is formed. The dextrin may, therefore, be looked upon as the original substance hydrolyzed, the maltose and dextrose as successive products of the reaction. Further, it has been shown that whatever the condition of the hydrolysis of starch by acids, the specific rotatory power of any conversion product corresponds to a definite chemical composition, tables for determining which have been constructed.

Thus, for instance, a conversion product of  $(\alpha)_D 160^\circ$  has been shown to contain 54% dextrin, the remainder being maltose and dextrose. Hence the time of taking any sample after the contents of the autoclave have reached a constant temperature, which requires about 10 minutes, can be taken as the initial point for determining speed of hydrolysis and all subsequent samples referred to this, as it is obvious that in any sample we can ascertain the dextrin unacted upon at that stage of the hydrolysis. The same holds true of maltose.



We have to deal with two reactions, the first being the hydrolysis of dextrin to maltose.

If  $A^\circ$  is the amount of dextrin at the initial point taken,  $A^\circ - x$ , the amount remaining at any time  $t$ , and  $c$ , the constant depending on conditions of hydrolysis we get  $\frac{dx}{dt} = c (A^\circ - x)$ .

This, on integrating gives  $\text{nat. log. } \frac{A^\circ}{A^\circ - x} \text{ ct, or } \frac{1}{t} = \text{nat. log. } \frac{A^\circ}{A^\circ - x} = C$ , which is the general equation of a first order reaction.

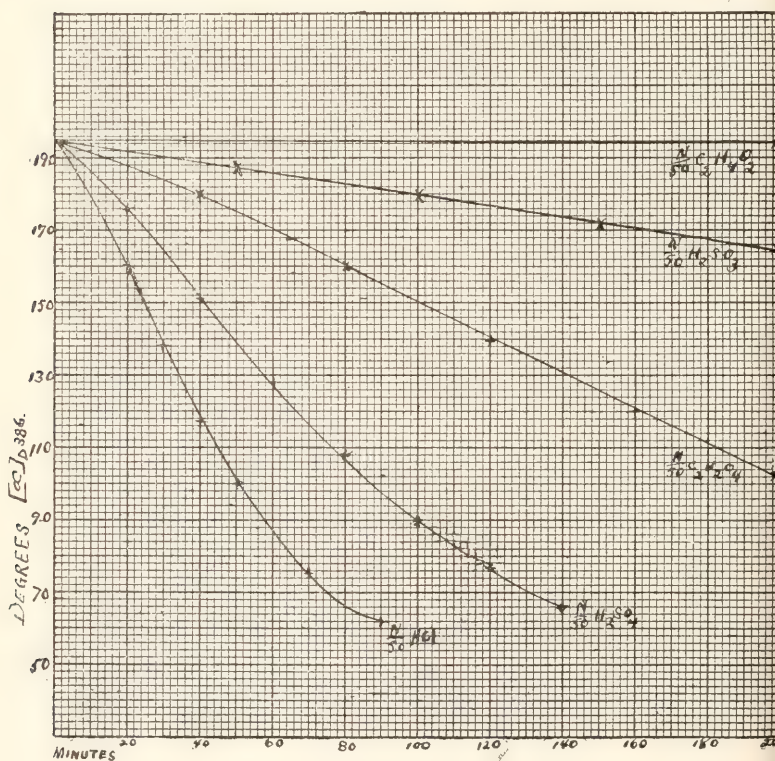


PLATE C.  
INFLUENCE OF VARIOUS ACIDS

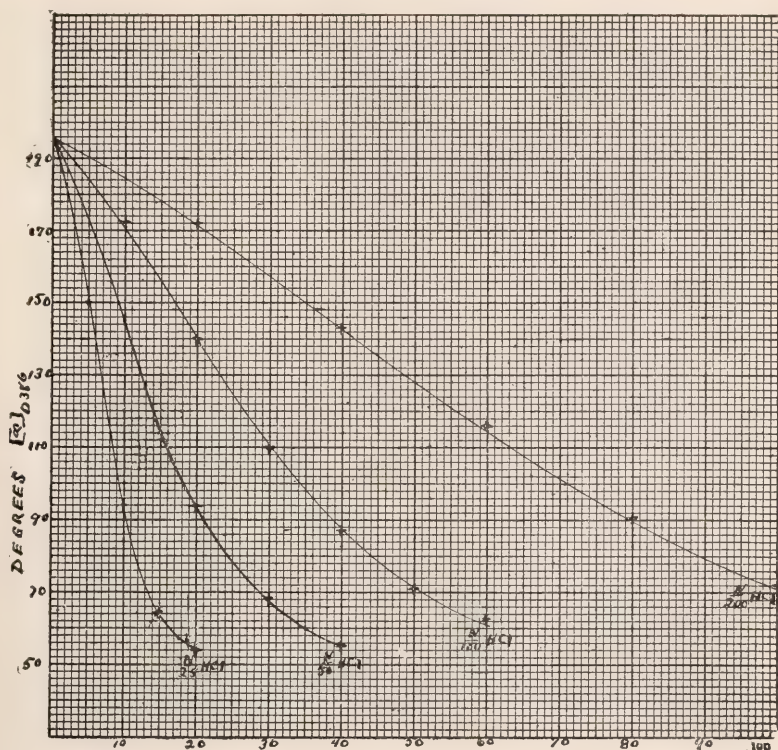
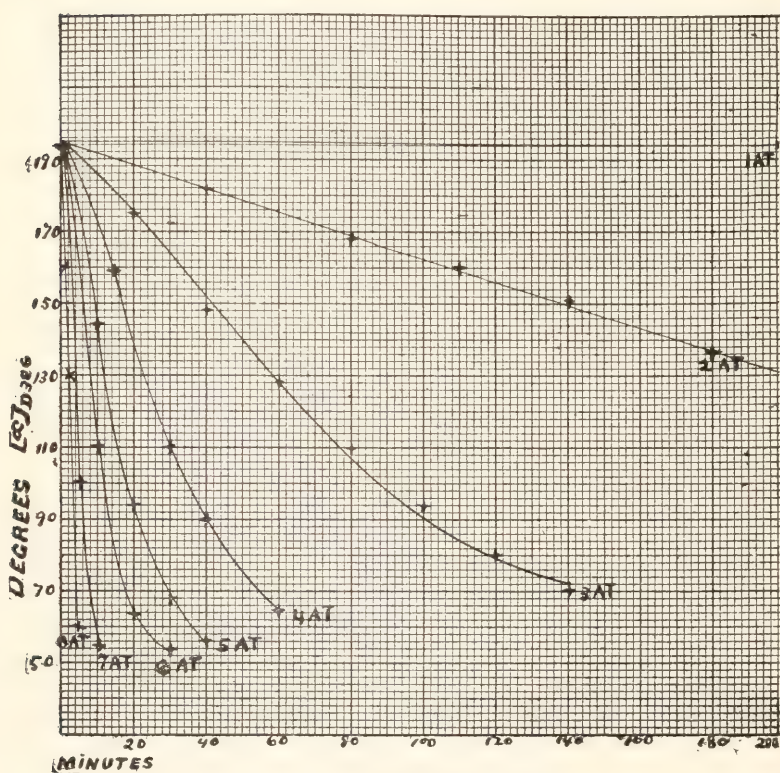


PLATE D.  
INFLUENCE OF STRENGTH OF ACID AT 44°C (114.5°C).

The second decomposition is that in which maltose is hydrolyzed to dextrose, and is peculiar in so far as it proceeds simultaneously with that reaction expressed by the equation above. Consequently the equation expressing accurately the rate of change in the total amount of maltose present is quite complicated, and this has led to the use of an approximate formula, which is sufficiently exact for the work in hand. The formula is derived from the exact differential equation  $\frac{dD}{dt} = CM$ , which states that the amount of dextrose formed at each moment is proportional to the amount of maltose present, by replacing the differential

quantities by finite differences, which, in application of the formula, must of course be taken small. In the place of  $M$ , the average amount of maltose present during the interval of time considered is also substituted. That is, if  $M_1$  and  $M_2$  are the amounts of maltose present at the times  $t_1$  and  $t_2$ , and  $D_1$  and  $D_2$ , the amounts of dextrose present at these same times, and  $c_1$  the reaction constant, we get as a result of the above-mentioned substitutions:

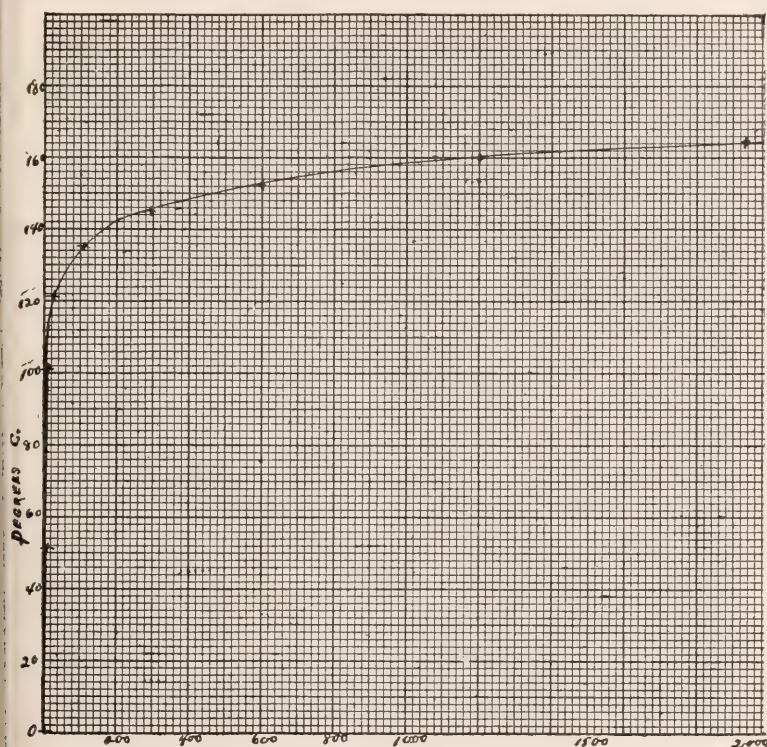
$$D_2 - D_1 = c_2 \frac{M_1 + M_2}{2} (t_2 - t_1), \quad C_1 \left( \frac{1}{t_2 - t_1} \right) \left( \frac{D_2 - D_1}{\frac{M_1 + M_2}{2}} \right) = C_2.$$



### PLATE E

INFLUENCE OF TEMPERATURE  $\frac{N}{100}$  HCl.





### PLATE F.

INFLUENCE OF TEMPERATURE ON RELATIVE SPEEDS OF  
HYDROLYSIS.  $\frac{N}{100}$  HCl AT  $134^{\circ}\text{C}$  [3AT] = 100.

Details of values and calculations have been omitted, as reference has been made<sup>1</sup> to an earlier article dealing with this problem, but it was felt necessary to include some of the former results in this paper as they had a bearing on the work in hand. The original work has been extended to include values obtained at lower as well as at higher temperatures, and it is now given as a whole.

Relative speeds of hydrolysis have been recalculated to a basis referred to that  $\frac{N}{100}$  of HCl at  $134^{\circ} = 100$ .

The summary of results is given in the following tables:

Table I shows the influence of the various acids on the speed of hydrolysis at the same temperatures, in this case 134° C. See also Plate C.

Table II gives the influence of varying amounts of acids, at 145° C. See plate D.

Table III shows the influence of different temperatures, the amount of acid being constant. See Plate 6. The relative effects of temperature change are shown graphically in Plate F.

TABLE I

| Acid         | Concentration | Average $c_1$ | Relative speeds<br>$\frac{N}{100}$ HCl at 134 = 100 |
|--------------|---------------|---------------|---|
| Hydrochloric | 0.02 N        | 0.0234        | 200.  |
| Sulphuric    | 0.02 N        | 0.0118        | 100.7   |
| Oxalic       | 0.02 N        | 0.0048        | 40.8  |
| Sulphurous   | 0.02 N        | 0.0011        | 4.8   |
| Acetic       | 0.02 N        | 0.0002        | .8  |

TABLE II

| Acid         | Concentration | Average $c_2$ | Relative speeds<br>$\frac{N}{100}$ HCl = 100 |
|--------------|---------------|---------------|--|
| Hydrochloric | 0.005 N       | 0.0155        | 33.1   |
| Hydrochloric | 0.01 N        | 0.0314        | 67.0   |
| Hydrochloric | 0.02 N        | 0.0678        | 144.7  |
| Hydrochloric | 0.04 N        | 0.1413        | 301.4  |

TABLE III

| Acid         | Concentration | Pressure<br>Atmospheres | Temp.<br>°C. | Average<br>$c_1$ | Relative speeds<br>$\frac{N}{100}$ HCl at<br>134°C. = 100 |
|--------------|---------------|-------------------------|--------------|------------------|---|
| Hydrochloric | 0.01 N        |                         | 0°           |                  |   |
| Hydrochloric | 0.01 N        |                         | 50°          | 0.00001          | .1  |
| Hydrochloric | 0.01 N        | 1                       | 100°         | 0.0003           | 2.5   |
| Hydrochloric | 0.01 N        | 2                       | 121°         | 0.0028           | 22.8  |
| Hydrochloric | 0.01 N        | 3                       | 134°         | 0.0120           | 100.  |
| Hydrochloric | 0.01 N        | 4                       | 144°         | 0.0323           | 278.  |
| Hydrochloric | 0.01 N        | 5                       | 152°         | 0.0668           | 570.  |
| Hydrochloric | 0.01 N        | 6                       | 159°         | 0.0976           | 1171.2  |
| Hydrochloric | 0.01 N        | 7                       | 165°         | 0.1582           | 1898.4  |
| Hydrochloric | 0.01 N        | 8                       | 171°         | 0.2240           | 2688.   |



It was found that starch paste would hydrolyze with acids even at zero C. but the rate was too slow to measure with the polariscope, although the hydrolysis could be followed by Fehling's solution. At this temperature the action was extremely slow in comparison with that obtained at higher temperatures.

The starch molecule evidently becomes very "labile" at temperatures above 100° C. as is evident from the remarkable increase in the relative speed of hydrolysis with rise of temperature.

The curve in Plate F is found to have a logarithmic equation, expressed by the formula  $\log r = mt - c$ , which from the plot resolves to:  $\log r = 0.0444 t - 4.014$ , where  $r$  is the rate of speed and  $t$  the temperature centigrade.

I am greatly indebted to Mr. George W. Rolfe for much assistance and kindly criticism in this work.



## SOME SPECIAL ASPECTS OF STARCH

BY CHESTER B. DURYEA

*Brooklyn, N. Y.*

Natural or ordinary starch granules should be said to be or to constitute starch itself. Thus basically this substance is definable as the systems of essentially carbohydrate material comprising normal starch granules.

As an indication of the extent of variation in properties between various kinds of normal starches as naturally occurring with granules diverse in size, I cite a result from an investigation carried out by me about four years ago. Aqueous suspensions of potato and maize starches were acidified with hydrochloric acid and maintained at 45° C., at a gravity of 14° Bé, for considerable periods of time. Samples were systematically taken and examined. Acidities during treatments were 1.2 and 0.6 per cent HCl for the potato and maize starches, respectively.

The potential viscosity of the potato starch, at the outset, was of course far greater than that of the maize; so much so, indeed, that it was impracticable at the time to make a direct comparison that was satisfactory. Viscosimetric determinations on a uniform basis of concentration, conducted so as to follow the course of the hydrolysis, or modification, showed that for the same reduced viscosity in each case just coming within the range of the method used the potato starch required about four hours' treatment, as against one hour for the maize, although the former starch had been acted upon by an acidity twice as great as the latter. A useful system of intercomparison of starches could be developed along these lines, taking cognizance also of significant differences in modification curves, and it would be all the better for a correlation with it of the cupric-reducing powers of the washed granules, etc.

As regards new physico-chemical evidence respecting a heterogeneous structure of starch granules and of the quality of the structure, the following outline is offered.

I have found that acid hydrolyzed or modified starch granule products of the same general viscosity, produced in the one case by what I have termed the "in-suspension" process and in the other by the older "drying-in" method, react differently during their hydrolysis, and when finished show differences in their properties. For products carried well along in modification, in part these differences may be summarized, thus:

1. By the "drying-in" process a markedly greater percentage of the substance of the granules becomes soluble, although the general type of water soluble products remains much the same, as indicated by ratios of cupric reducing to apparent specific rotation values.

2. Of the two varieties of thoroughly washed products, that yielded by the "drying-in" process possesses much the greater specific reducing power.

Herein I can only suggest my explanation, which is indicated by the statement that I believe the differences between the "drying-in" and "in-suspension" results tend to prove a non-homogeneous, or selective, concentration of water and acid within the granules, wherein their substance is less compact and more hygroscopic, during the progress of the former process—thus because of inherent variations in the granule substance developing a differentiation from normal "in-suspension" conditions.

To a considerable extent, I have obtained evidence of a similar nature through comparisons of results from "in-suspension" treatments at 55° C., the normal incipient swelling point of maize starch granules, and treatments at 59° C., at which temperature there is material general swelling. This seems to take place in such a way as to relatively increase the condition of hydration, and so the hydrolytic susceptibility, in the very same parts of the granules within which water and acid appear to concentrate during "drying-in" procedure.

As regards the amylopectin hypothesis abandoned by its authors as untenable, but revived by Matthews and Lott in a greatly modified form (*J. Inst. Brewing*, 1911, pp. 219-270), it does not seem to me just to argue so exclusively from evidence secured in the main from diastatic or other reactions with starch pastes, however valid by themselves such evidences may appear

to be, for the reason that the matter primarily relates to the composition of starch granules.

Citing and discussing in this connection a single instance familiar to all, some work done by Brown and Morris (*J. Chem. Soc.*, 1889, 449), in the course of which potato starch granules were treated in the cold with moderately dilute mineral acid, seems to bear upon the amylopectin idea. At the end of  $8\frac{1}{2}$  years, these distinguished investigators found about 40% of the original granules appearing in solution as glucose, while the residual 60% remained in the form of granule débris, having the composition and properties of Nägeli's amyloextrin. My own general experience is to the effect that the more resistant portions of at least maize starch granules contribute very importantly to characteristic starch viscosimetric phenomena and to the production of primary maltose, and further that under suitable conditions of paste preparation these portions all yield the characteristic blue iodine reaction. This, as I understand the question, is contrary to the amylopectin theory, but is supported, I believe, by the work of Brown and Morris cited. It would certainly seem, in their experiment, as if the more easily attacked portions of the granules naturally must have been those which were converted into glucose, while the more resistant were represented by the residue. In view of the fact that the equivalent of the 40% of original carbohydrate in solution was all glucose, and of the circumstance that the 60% as residue was a single substance, all readily converted into maltose by diastase, and so easily carried into glucose, a conclusion appears manifest that, so far as the granules were concerned, the main differences between the various parts of their substance, and between the granules of different size, were those affecting solubility, and further that owing to the long time of treatment action had become so slow that the rate of conversion into glucose, of the matter dissolved, was greater than the rate of solution of the granules. The solid matter had also reached an equilibrium state of a single well defined substance, which because of its properties might well be said to be the lowest member of a simplifying series of true starchy extrins, and which as already stated was entirely converted by diastatic digestion into maltose—readily in turn transformed to



glucose, the sole carbohydrate found in the solution. To complete a train of ideas strongly in favor of a belief in a general chemical unity of the original granules, at this point attention should be invited to the further related fact that among the soluble products resulting from the acid hydrolysis of starch granules not glucose but maltose is the sugar first formed (J. Soc. Chem. Ind., 1911, 30, 789), and that this chemical individual continues to be the characteristic or constitutional sugar product for a very considerable portion of the hydrolytic course. In my own work with normally mixed maize starch granules modified by the "drying-in" process, I have traced this last mentioned condition as obtaining to a point where 9.0% of the original granules had become soluble. At this stage the combined water extracted products had the constants  $[\alpha]_D^{20} = 192.4^\circ$  and  $R = 14$ , both values being references back to an original anhydrous starch equivalent of the carbohydrates in solution. The phenylhydrazine acetate test on the mixed products yielded abundant maltosazone, but gave entirely negative results for glucose.

So much space has been given over to sketching aspects of starch as starch, that is, as starch granules, that the remainder of this paper must be very brief.

I would, however, like to confirm recent evidence (Fernbach and Schön, J. Soc. Chem. Ind., 1912, 402) to the effect that "there is no reason to consider that the acid saccharification of starch proceeds differently from the diastatic, at least, during its earlier stages", by the statement that I have found through extended experience with normal and modified maize starch granule pastes, under conditions of very low acidity and high concentration (as high as 36%), that, up to a stage short of the formation of any considerable relative amount of glucose, there is apparently no profound divergence in normal acid hydrolysis from the general results characteristic of physiological or enzymic digestion.

Pastes other than aqueous, such as pastes with solutions of alkalies, chloral hydrate, various deliquescent salts, etc., have been considered to be outside of the scope of this paper.

With regard to the synthesis basic to starch formation, we all know that protoplasm, chlorophyll, light and carbon dioxide are involved. After starch is once formed, translocations with re-

deposition of granules take place without intervention of chlorophyll and light.

In this connection, I would suggest the idea of a special biological condition or field, dynamically actuated by electro-magnetic light. Applied to the starch manufacturing chlorophyll cells of plant leaves, my thought may be outlined as follows:

1. Because of the colloidal and stable character of the chloroplasts, the condition of existence of water therein, and the general and specific properties of carbon dioxide in relation thereto, when molecules of this gas are first taken up from the atmosphere they may be to an extent somewhat loosely held rather than firmly bonded chemically.

2. The conditions of absorption of the  $\text{CO}_2$  molecules, by the colloidal chloroplasts, enormously reduces the rate and amplitude of their general motions even as compared with solution in water, and brings them within the range or sphere of the specific influence of the wave fronts of light.

3. These circumstances introduce the carbon dioxide complexes under conditions of existence within a reacting system of chloroplasts and light, in such wise that they may become caught by or engaged with this specific mechanism of active fluorescence, and thus become unstable. Decomposition would ensue, accompanied by the formation of new carbon compounds. The carbohydrate type of these new bodies might be facilitated if the light action also aided in depolymerizing some of the water present.

This idea of special colloidal fields, I believe, may apply very generally to vital processes, as providing for a more intimate and specific relationship between molecules than exists in the ordinary states of solutions.

With regard to a general bio-chemical formula for starch, it seems to me that no evidence may be valid except it is secured under circumstances which are compatible with the conditions of starch synthesis, and consistent also with the known conditions and facts connected with the reversibility of biological translocations of this substance. Of the formulas proposed, it therefore still seems best to prefer for the present that advanced by A. R. Ling, in 1909 (VIIth Internat. Congress App. Chem., Sec. VI B, p. 123), which in a little different form may be written  $(\text{C}_6\text{H}_{12}\text{O}_6)_n - (\text{H}_2\text{O})_{n-1}$ .



# SUR UNE NOUVELLE FORME D'AMIDON SOLUBLE

PAR M. A. FERNBACH

*Professeur à l'Institut Pasteur de Paris*

(Note préliminaire)

M. G. Malfitano et M<sup>lle</sup> Moschkoff ont montré récemment (*Comptes rendus de l'Académie des Sciences*, 12 février 1912) que de l'amidon déminéralisé, préparé par leur méthode de congélations successives, se dextrinise en devenant peu à peu soluble lorsqu'on le soumet à la dessiccation, c'est à dire par déshydratation. Ce résultat nous a suggéré l'idée de transformer de l'amidon en sa forme soluble par l'action de déshydratants, parmi lesquels nous avons essayé tout d'abord l'alcool absolu et l'acétone pure. Nous nous bornons à mentionner dans la présente note les résultats obtenus avec l'acétone, sur laquelle ont surtout porté nos expériences.

Si on verse dans un grand excès d'acétone pure de l'emploi d'amidon à 1 ou 2%, préparé avec de la fécule de pommes de terre du commerce, c'est à dire n'ayant subi aucun traitement préalable pour sa déminéralisation, on obtient un précipité floconneux, qui se forme au fur et à mesure que l'empois tombe en mince filet dans l'acétone fortement agitée.

Le précipité, recueilli sur un entonnoir de Buchner, est broyé dans un mortier avec de l'acétone pure, essoré et séché dans le vide sec. On obtient ainsi une masse parfaitement blanche, pulvérulente et très légère, qui présente cette particularité très intéressante d'être soluble, non seulement dans l'eau chaude, mais aussi dans l'eau froide. Deux grammes de cet amidon soluble se dissolvent facilement à froid dans 200 centimètres cubes d'eau, en ne laissant comme résidu insoluble qu'une fraction infime de la masse primitive.

L'amidon soluble obtenu par la méthode que nous venons de décrire présente sur les amidons solubles préparés par les procédés indiqués jusqu'ici l'avantage appréciable d'être totalement

dépourvu de pouvoir réducteur. Il se saccharifie facilement par l'extrait de malt, exactement comme l'empois d'amidon qui a servi à le préparer. Sa solution, qui filtre facilement sur du papier, se colore par l'iode en bleu pur intense.

L'obtention d'un amidon presque intégralement soluble à froid exige qu'on emploie pour sa préparation un empois dilué. Si on dépasse pour cet empois la concentration de 2%, on obtient un produit qui n'est que partiellement soluble à froid; on peut séparer la portion soluble par filtration sur du papier, bien que cette filtration soit très lente, et ce qui reste sur le filtre a un aspect tout à fait comparable à celui de l'empois d'amidon.

Nous avons constaté que si on précipite par l'acétone ou par l'alcool une solution préparée à chaud d'amidon soluble obtenu par la méthode de Fernbach-Wolff (*Comptes rendus de l'Académie des Sciences*, 15 Mai 1905), lequel est absolument insoluble à froid, on obtient, à la suite d'une agitation énergique, un précipité floconneux, qu'on arrive à séparer par centrifugation, et qui, après séchage dans le vide sec, se dissout intégralement dans l'eau froide, mais en donnant une solution moins limpide que l'amidon soluble obtenu par précipitation d'un empois dilué au moyen de l'acétone.

Les solutions de la nouvelle forme d'amidon, soluble à froid, présentent, comme l'empois qui a servi à le préparer, la propriété de subir le phénomène de la rétrogradation.

Les recherches brièvement exposées dans ce qui précède ont été exécutées avec l'aide de M. M. Schoen, auquel nous exprimons ici tous nos remerciements pour son concours précieux.



## THE CHEMISTRY OF STARCH

By G. B. FRANKFORTER

*University of Minnesota, Minneapolis, Minn.*

Starch is the most important member of the group of organic compounds commonly known as the carbohydrates. It is not as abundant as its sister compound, cellulose, but the rôle which it plays in both plant and animal life easily places it in the front rank. It has been known to the human race for centuries. The early history of the science of chemistry shows that those substances which exist free in nature, or those substances which are easily prepared, were the first to be studied and used. Starch is easily prepared from the various cereals and very easily from tubers, like the potato. Starch was doubtless first prepared from wheat grown in Mesopotamia, in Palestine and in Egypt. Dioscorides about the middle of the first century of the Christian Era gives the first account of its preparation from wheat. From his meagre descriptions of this, and other early industrial chemical and mechanical processes, and from the fact that many of these processes doubtless required some special chemical knowledge and mechanical skill, one may, I think, conclude that some of these processes must have developed very slowly and that starch and possibly sugar must have been prepared centuries before the Christian Era. It is evident, however, that neither starch nor sugar could have been prepared in large quantities, for both during the early centuries were regarded as luxuries.

From what has been handed down concerning the early preparation of starch, there seems to be little doubt but what it was obtained in much the same way as it is prepared today, the chief difference apparently being that the machinery used for each succeeding generation has improved, so that it could be prepared in purer form and in larger quantities. At any rate, starch has long since changed from the luxury class to the most important of all of the foodstuffs.

Starch is widely distributed in both the plant and the animal world. It occurs in all plants in greater or less quantities, for it

seems to be formed whenever chlorophyll is exposed to sunlight. Bulkewitsch (Biochem. Centr. 10-314) found that starch was the first carbohydrate formed in *Morus alba* and *Saphora japonica*. He does not, however, state that it was formed through the action of chlorophyll, but quite the contrary. He found that twigs of the above species when kept at room temperature for some time produced starch, and attributes its formation to enzymes, starch, however, being the first carbohydrate formed. While this and other experiments along the same line are important, the evidence at present is certainly not sufficient to prove that in all cases starch is the first carbohydrate formed in plant growth. Incidentally, it was shown by Bulkewitsch that while starch is formed by enzymic action, there are either several varieties of enzymes or the same become inactive under different conditions.

Another interesting reaction is the change produced by hydrogen peroxide (Comp. rend. 148-578). Common starch, glycogen and inulin undergo both hydrolysis and oxidation in the presence of small quantities of hydrogen peroxide. Whether the small quantity of hydrogen peroxide in the air plays a part in the chemistry of the starches and sugars is certainly a problem worthy of careful experimentation. Starch is present in plant growth from the time the seed begins to germinate until the plant has reached maturity. It is in all seeds and especially in the cereals, where it is stored up for the purpose of supplying the young plant with food until it is large enough to produce its own supply.

But starch is by no means confined to the plant world. Its importance in the animal world is now a matter of common knowledge although the chemical processes involved in its formation are by no means clear. In a modified form, commonly known as glycogen, it doubtless plays much the same part in the physiological chemical processes that common starch does in plant growth if all its functions were known. It appears to be formed from common starch by enzymic action.

*Physical Properties.* Starch from any one of the great sources when pure is of a very light creamy white color with no odor and no taste. Its specific gravity is given as 1.505, although under certain conditions it may be as high as 1.59. Potato starch turns red litmus paper blue, according to some authors, but as a general

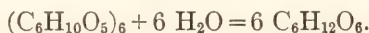
rule the reaction is neutral. While starch from the various species of plant seem to have the same general properties, it requires but a glance to show that almost every family of plants has its own peculiar form of starch granules. The difference is entirely physical and doubtless means simply different aggregation of molecules which go to make up the granules themselves. Thus while wheat and corn starches apparently have the same molecular form and structure, these molecular aggregations or granules are so different in size and shape when examined under the microscope and especially in polarized light, that the chemist familiar with these different forms finds no difficulty whatever in identifying the source of any of the common forms.

*The Chemistry Proper of Starch.* The development of starch chemistry has been very slow, taking into consideration its importance and the vital part which it plays both in plant and animal life. Probably no other great important organic compound, not even excepting its complex sister compound, cellulose, has been so little studied from the purely chemical point of view as starch. A casual glance into the history of organic chemistry and especially that branch known as phytochemistry, reveals the fact that with few exceptions the mass of chemical work has been confined to compounds which have distinct crystalline forms, or else admit of purification by some more or less simple process. This is doubtless one of the reasons why the complex compounds like the alkaloids began to be studied nearly a century earlier than the common and more important substances like the sugars, starches and celluloses. During the last quarter of a century hundreds of chemists have worked more or less closely with the carbohydrates, but Kiliani, Tollens, Emil Fischer, Cross and Bevan and perhaps half a dozen other investigators would include practically all the men who really succeeded in obtaining from this most important group of compounds distinctly positive results. As a matter of fact, the molecular constitution of the starches and the resins have, up to the present time, seriously occupied the attention of but a very few, most chemists regarding them as too complex for serious consideration. The wonderful work of Fischer, Tollens, Wohl and others on the sugars, however, leads one to believe that in the not very distant future the constitution of all of

the common sugars as well as starch and cellulose will have been worked out, and the molecules built up from simple forms like formaldehyde and its polymerized derivatives, the simple hexoses.

The first really important chemical work on starch which I have been able to record was done by Kirchhoff in 1811 (*Schweigger's Journal*, 4-108). Kirchhoff showed that when starch is heated with dilute acids it dissolved, and on removing the acid and the water the substance remaining was no longer starch, but a mixture of several substances belonging to the sugar group, among them the well-known substances dextrine and dextrose. A few years later the same investigator showed that similar substances were formed when starch was subjected to certain forms of fermentation which, from his description, must have been identical with modern diastatic action. These, like many important chemical reactions, were not regarded as important at the time of their discovery. It was more than a half century after Kirchhoff's observations that the importance of his discovery was fully appreciated and made use of commercially. The breaking up of the starch molecule by boiling water is another phenomenon which until recently was practically unknown, although it must have been observed for several generations.

What happens molecularly in these hydrolytic reactions is largely a matter of speculation, for while various more or less conventional equations may represent what changes take place, it is obvious that only the most general equation will indicate what changes really occur when starch is hydrolyzed either by boiling water or by acids. In the former case dextrine is largely formed, while in the latter the final product is dextrose. Assuming that the reaction is complete, it may be represented by the following:



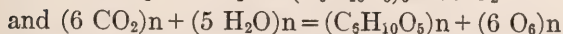
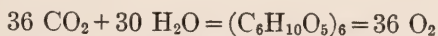
The above formula for starch is based on early investigations especially of starch iodide. The size of the starch molecule evidently cannot be determined with accuracy from the iodide, as different investigators have obtained results varying from  $(\text{C}_6\text{H}_{10}\text{O}_5)_2$  to  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$  when  $n$  is greater than 6. From the writer's experience and the results obtained by several investigators, the hexapolymer seems to have a slight preference over



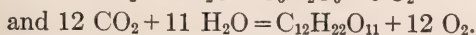
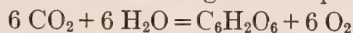
either  $(C_6H_{10}O_5)_2$ ,  $(C_6H_{10}O_5)_4$  and  $(C_6H_{10}O_5)_6$ . It must be remembered as pointed out by Ling (Seventh Int. Cong. of App. Chem., London, 1909), that these and the formulæ presented in this paper are only attempts to formulate some of the chemical facts concerning starch.

*Synthesis of the Starch Molecule.* A. W. v. Hofmann, I think, was the first to show that formaldehyde played an important role in the building up of the complex phytochemical compounds like sugar, starch and cellulose. Difficulties arose in his attempt to explain the synthetic action because, while he assumed formaldehyde to come from carbon dioxide, he regarded it as existing only in the hydrated form, which somewhat complicated the common polymerization theory. Hofmann also failed to prepare formaldehyde directly from carbon dioxide. Since Hofmann's time, however, formaldehyde has been prepared by the action of sunlight on carbon dioxide (Trans. Chem. Soc. 1907-91-687). Thus when carbon dioxide is passed into water in which has been placed metallic magnesium, some of the gas is reduced to formaldehyde. For conversion of formaldehyde into the sugar group, see Loew's and Butlerow's works on formose and methylenitan. Baeyer (Ber. 3-67) went farther and laid the first solid foundation upon which the carbohydrate synthesis might be built, by giving very general exposition of what takes place in the formation of the carbohydrates, especially starch and cellulose in the following equations:

$6 CO_2 + 5 H_2O = C_6H_{10}O_5 + 6 O_2$ . This equation may be enlarged so as to indicate the complexity of starch or cellulose by the following:



Or in the case of the sugars the equation may be as follows:



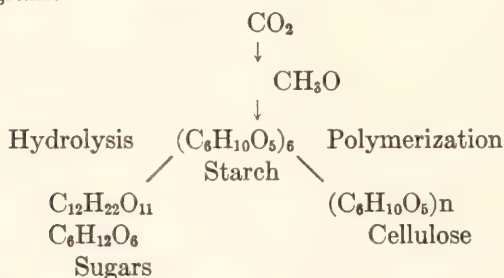
What these equations represent even at the present time is simply that certain chemical changes take place and that certain compounds are formed. They are not presumed to explain either the intermolecular changes which take place or the direction in which the reaction always proceeds. Considerable data has been



already obtained, but not sufficient to determine with accuracy the direction of the reaction in all cases.

Logically followed out, one would assume that synthetic reactions always proceed from the simple to the more complex, in which case formaldehyde would pass to polymers if two, three and six molecules, as for example, para formaldehyde, trioxymethylene and the hexoses, as formose and methylenitan. Then, again, by a dihexa and a polyhexa-polymerization it changes to the disaccharides and finally to the starch and cellulose groups. However vague these assumptions may seem, they do represent from the purely logical point of view, the most plausible explanations of facts concerning these important compounds.

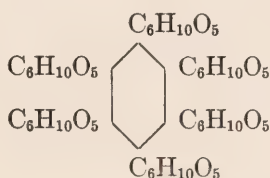
Facts, however, do not in all cases bear out the theory. The fact that starch is the first carbohydrate to appear in the leaves of plants by action of light on chlorophyl is difficult to reconcile to the progressive theory given above. Payen (*Compt. rend.* 53-813) showed beyond a doubt that not only green fruit but also the plants themselves, including the leaves, contain an appreciable amount of starch. Starch would seem to be, at least in certain plants, the first carbohydrate formed, so that in the formation of cellulose and grape sugar there is further polymerization on the one hand and hydrolization on the other, as indicated by the following diagram:



That experimental evidence at the present time is too meagre to attempt even to trace the details of the changes which take place in the formation of starch, is self-evident. Baeyer's theory in general seems to come nearer to the facts than any other thus far presented. Some phytochemists, however, are inclined to modify the theory, holding as indicated above that not only all carbo-

hydrates but all compounds, like the resins, gums, essential oils and terpenes, are direct derivatives of starch.

If these phytochemical facts are accepted as having a bearing on the starch molecule, they would tend to give starch a complex ring structure, as most of these substances as the resins, the gums, the terpenes and essential oils are ring compounds beyond a doubt. Following out this line of reasoning, Kronstein represented the resins which he regarded as direct derivatives of starch as ring compounds. If the starch molecules were constructed from Kronstein structural formula for the resins, the generally accepted starch molecule  $(C_6H_{10}O_5)_6$  would have the following formula, in which each group or starch unit is joined to its neighbors as explained in the aldehyde polymerization.



Cross and Bevan (Ber. 42-2198) in their application of Traube's theory of the relationship between the molecular volume and molecular solution volumes of compounds and their molecular weights, found that the molecular solution volumes of both starch and cellulose are lower than calculated by Traube (Ann. 290-43). They suggested that the low numbers were probably due to certain molecular arrangement, possibly to ring structure. Traube, himself, was requested by the authors to present his views on the subject and in a short review of the work suggested that the only way to explain the discrepancies was by the ring theory.

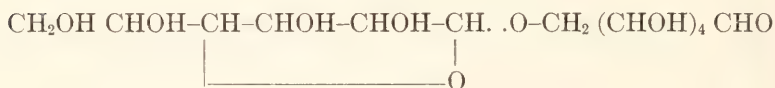
It does not follow from the above statement that the ring compound is used in the same sense that it is when applied to the aromatic compounds which are characterized by their great stability. It is more likely to be a polymerized form of the aldehydes which may be represented by a ring form.

The only other evidence which I have found concerning the ring form for starch is the fact that the resins are ring compounds

and the resins have been assumed to be direct derivatives of starch. The writer's work on the resins, however, indicates that the resins come from the terpenes rather than from starch, therefore to assume that the complex resin molecules come from starch is to assume that the terpenes themselves are produced from starch. The change of the starch molecule into a ring compound and its oxidation into the resin acids would be such an unusual chemical change as to require a large amount of experimental evidence to verify it.

The synthesis of the starch molecule it would seem to me should come from the sugars proper, although the appearance of starch as one of the first of the common substances formed in plant growth is rather an important evidence and favors starch formation without passing through the simpler sugar groups. Be the synthesis as it may, the relationship between the sugar and the starch molecules is very close, no matter whether the reaction proceeds from the simpler to the more complex or *vice versa* in plant growth.

From Fischer's work on the sugars and his structural formulæ for some of the disaccharides, it seems more probable that a reaction similar to the condensation of the mono to the disaccharides and the condensation of the di to the polysaccharides, comes nearer representing what actually takes place in plant growth than the starch and especially the starch ring theory. Thus a disaccharide may be represented as derived from the monosaccharides by the following condensation:



By continuing these condensations, compounds of two, three or more of the mono or hexahexose molecules may be formed, as for example,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ,  $\text{C}_{12}\text{H}_{32}\text{O}_{10}$ ,  $\text{C}_{24}\text{H}_{42}\text{O}_{21}$  and  $\text{C}_{36}\text{H}_{62}\text{O}_{31}$  or  $\text{C}_{36}\text{H}_{60}\text{O}_{30}$ . By following out the Fischer condensation idea, a starch molecule of any size may be built up. Even Geinsberghens molecule for cellulose  $(\text{C}_6\text{H}_{10}\text{O}_5)_{34}$  lies quite within the reaction limit.

Wacker (Ber. 41-266) has succeeded in determining the complexity of the starch molecule in terms of the hexose groups. The method employed depends upon the fact that p. phenylhydrazine sulphonic acid and other hydrazines produce with aldehydes and alcohols by the aliphatic series, in the presence of excess of alkalies, an intense red color. The dye formed varies very little with the different carbohydrates, at least not sufficiently to interfere with the use of the method. He formulated the following law that the color intensity decreases with increase in molecular weight. By working out some thirty or forty different compounds, he obtained data such as would enable him to determine the molecular weight of the complex as well as the simple carbohydrates.

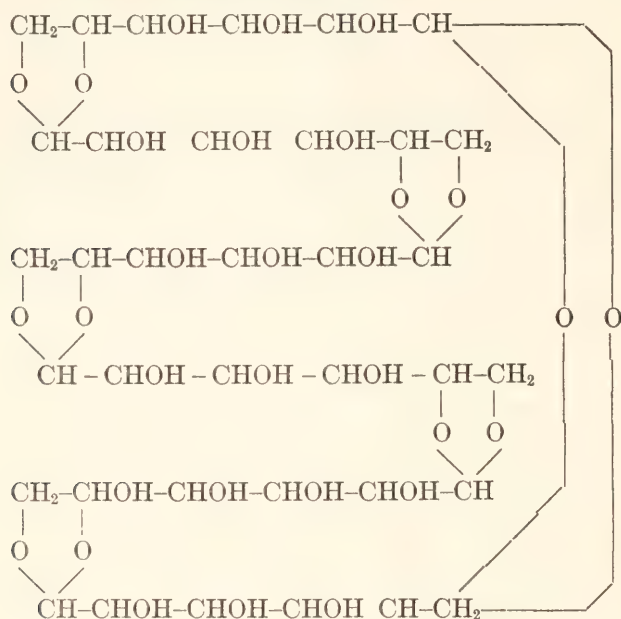
Later (Ber. 42-2675) he extended his experiments to starch. He found the number of hexose groups to vary from 5 to 8, giving for the less soluble granulose the mean, or six groups in the molecule. Glycogen, although it has generally been accepted as having a smaller molecule than common starch, was found to vary, but on the whole he found it to be more complex, the number of groups being approximately 10.

The following is a table of the different forms of common starch:

|                                   |                 |
|-----------------------------------|-----------------|
| Very soluble starch . . . . .     | 5 hexose groups |
| Difficultly soluble . . . . .     | 6 hexose groups |
| Once dissolved . . . . .          | 7 hexose groups |
| Several times dissolved . . . . . | 8 hexose groups |

The fact that dextrine contains the aldehyde groups (Ber. 23-3060) indicates that the aldehyde groups are no longer neutralized by polymerisation, but have been liberated by hydrolysis on the one hand, and perhaps a splitting off of a part of the starch molecule on the other, dextrine being first, and dextrose finally formed by complete hydrolysis. Thus if starch is represented by condensed hexahexoses, by following out Fischer and Ladenburg, the molecule may be represented by the following:





It must not be construed that these formulæ mean anything more than an attempt to apply certain known facts to the starch molecule. Apparently, the starch molecule is at least of the above size, probably greater than the hexa form. It contains no aldehyde groups, but by hydrolizing it is readily converted into dextrine, which may be represented by breaking one of the hexa groups and the taking on of a molecule of water to form an aldehyde. At any rate, it probably comes nearer to the general structure of the starch molecule than the old generally accepted formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ .

*Glycogen.* The chemistry of starch would not be complete without at least a brief *résumé* of some of the modified forms of starch, as glycogen and inulin. Common starch, as the term is ordinarily understood, seems to be produced in the plant world only, but as there are many different sugars, so there are doubtless many different starches. The starch which occurs most abundantly in the animal world is known as glycogen or animal starch. Glycogen occurs in both the herbivorous and carnivorous animals, especially



in the liver and heart. Its origin is not entirely clear, although there seems to be little doubt but what it is formed largely from common vegetable starch notwithstanding the fact that it appears quite as abundant in the carnivorous as it does in the herbivorous animals. Its composition is still unsettled, but from its combination with barium hydroxide, forming a well characterized compound  $(C_6H_{10}O_5)_5 Ba (OH)_2$ , (Arch. f. d. ges. Physiol. 37-582), the molecule appears smaller than the common starch molecule, the result of either a partial breaking down of common starch through metabolic changes or through partial hydrolysis. Glycogen is readily prepared from the liver by treating the organ with hot water and allowing to stand for some time, then filtering and precipitating out the glycogen with alcohol.

Glycogen in some respects resembles common starch, while in others it differs widely. It is soluble in water, thereby differing from common starch. It has about the same specific gravity. In solution it is optically active, turning the plane of polarization strongly to right,  $(\alpha)_D + 200^\circ$  or nearly four times more active than dextrose. Its identification and separation from common starch are due to the fact that it dissolves in water with a peculiar opalescence, while starch is insoluble and naturally does not produce the opalescence. It differs from starch in its reducing power after having been hydrolyzed by acids and from the fact that it is converted by ferments directly into dextrose. It forms with iodine, in the presence of sodium chloride, a reddish brown solution, and with benzoyl chloride and sodium hydroxide a well characterized, while powdered benzoyl glycogen (Zeit. f. Physiol. Chem. 13-125). Treated with potassium hydroxide it is slowly decomposed. With common mineral acids it reacts not unlike starch, changing to dextrine, then to maltose and finally to dextrose. A similar change takes place by diastatic or pancreatic action.

As has already been stated, the chemical changes which take place in the formation of glycogen are by no means clear. That the change of whatever nature is complex and deep-seated, probably involving a series of unidentified substances with the general characteristics of starch, is evident from the experiments of various writers. Thus Naegeli (J. 1859-544) has shown that in the change of common starch to glycogen, several compounds mostly unidenti

fied are formed in the intermediate stages between common starch and glycogen.

Daresto (Compt. rend. 72-845) found that the yolk of freshly layed eggs contains a substance with the granular appearance and with many of the characteristics of common starch, being optically active and giving the blue starch iodide reaction in the presence of iodine. A study of eggs after incubation indicates that three and perhaps four compounds are formed in the change of starch to dextrose. In fact, Daresto found during the stage of incubation that there were successive changes from starch to dextrose, and *vice versa*, so that the common reaction given for the change of starch to dextrose may be made reversible and as follows:



The writer has verified many of these experiments and therefore believes that there is at least one intermediate substance of starchy nature between starch and glycogen.

Schutsenberger (Ann. Chem. Pharm. 140-74) has shown that acetic anhydride not only combines with starch to form a well characterized triacetyl derivative but also with glycogen, forming a somewhat similar triacetyl compound. These acetyl compounds are very important in the identification of the respective starches. The writer believes that the acetyl and benzoyl derivatives will prove to be of more importance in the working out of the constitution of the starches than any other reactions known at the present time.

*Inulin.* Inulin, another form of starch, is distributed through a large group of plants in which it evidently plays the part of common starch. It is readily obtained by digesting the material containing the inulin with hot water. It is again precipitated on cooling. It resembles starch very closely in its general physical properties, but in its chemical properties it differs widely. While it seems to take the place of starch in certain cases, its function must be different, inasmuch as it exists in plants in the form of a solution, which necessitates different functions. In the solid form it is very hygroscopic, taking on water more rapidly than starch under the same conditions. It is slightly soluble in cold water

but quite readily in hot, from which it separates out on cooling in the form of a powder. Heated with water or dilute acids, it changes to *lævulose*. It is colored brown by iodine, thus resembling glycogen. It is a powerful reducing agent, readily precipitating copper and silver from their salts. Little is known of its constitution, but according to the work of Tanret (*Compt. rend.* 116-514 and *Bul. soc. chim.* 9-227) who has studied several of the starchy compounds including inulin, pseudo inulin and inulenin, the size of the inulin molecule is the same as the formula given for common starch, namely  $(C_6H_{10}O_5)_6 \cdot H_2O$  or  $C_{36}H_{62}O_{31}$ , notwithstanding that a molecular weight determination by the Raoult method gave numbers which agreed with penta instead of the hexa polymer.

In conclusion, it should be stated that some of the important references have been omitted because they have been referred to in a general *résumé* of starch chemistry in the proceedings of the previous congresses. The whole paper, therefore, had to be modified on this account.

The writer desires to state in conclusion that he believes starch offers more opportunities to the chemist for important discoveries than any other group of compounds in the whole realm of organic chemistry. Not only is the chemistry proper of vital importance as offering an almost boundless field, but also the great vital subject of fermentation which is so closely connected with the starch. It is to be hoped that in the near future chemists may give more of their time to the chemistry of starch and especially fermentation. If chemists or botanists with a thorough knowledge of chemistry should devote more of their time to the study of starch, the next decade would see the chemistry of starch completely rewritten.



## HYDROLYSIS OF CELLULOSE AND LIGNO CELLULOSE

BY F. E. GALLAGHER AND I. L. PEARL

*Boston, Mass.*

When wood or sawdust is cooked at high pressures with dilute acids there is formed a considerable amount of fermentable sugar, mainly dextrose. Previous investigators have differed in their opinions as to the source of the sugar, some maintaining that it is formed from the cellulose and others from the lignin. The purpose of the experiments here described is to supply additional data that will contribute to the solution of the problem.

All of the cooks referred to in this paper were made on long-leaf pine sawdust screened through a 10-mesh sieve. As hydrolyzing agent 1%  $\text{H}_2\text{SO}_4$ , figured on the dry weight of the sawdust, was used. Three parts of liquor, by weight, were used for each part of sawdust. The cook was carried out in a porcelain lined covered dish suspended over water in an autoclave. A maximum pressure of 135 pounds (9 atmospheres) was maintained for thirty minutes. The total duration of the cook, including heating up and pressure relief periods, was about 70 minutes. The cooked sawdust was completely extracted by water, evaporated to about 11° Brix (1.045 Sp. gr.) and fermented. The percentages of water soluble and copper reducing materials were determined on portions of the evaporated extract.

A series of cooks was made to determine the extent to which fairly pure forms of cellulose could be converted into sugars by this procedure. The character of these experiments and the results will be clear from Table No. 1.

These results would indicate that pure cellulose can be converted into fermentable sugars. Cotton cellulose does not give as high a sugar yield as the wood celluloses under the hydrolyzing conditions used. Each of the celluloses is capable of yielding a further amount of sugars on re-cooking, and the extract from the second cook is the more fermentable. Contrary to the data of some previous investigators, the celluloses gave lower yields of soluble material and fermentable sugars than wood. The ratio of fer-



TABLE NO. 1  
SUGARS FROM PURE CELLULOSE MATERIAL

|   | Total<br>Extract | Reducing<br>Material | Fermentable<br>Sugars | Ratio<br>Fermentable<br>Sugars<br>Total Solids |
|---|------------------|----------------------|-----------------------|--|
| 1a Bleached Cotton  | 3.1%             | 1.6%                 | 1.4%                  | .44  |
| 1b Bleached Cotton (Resi-<br>due from 1a recooked)            | 4.5%             | 2.8%                 | 2.5%                  | .55  |
| 2a Bleached Soda Wood<br>Pulp                                 | 17.7%            | 16.0%                | 6.3%                  | .36  |
| 2b Bleached Soda Wood<br>Pulp. (Residue from<br>2a recooked.) | 7.5%             | 4.3%                 | 3.8%                  | .51  |

*Note.* To avoid burning, cottons were cooked at 100 lbs. instead of 135 lbs. per lb.

mentable sugars to the total soluble material is about the same as for extracts from wood cooks.

At ordinary temperatures, chlorine vigorously attacks the lignin portion of wood but has little effect on the cellulose portion. This is used as the basis of several analytical methods for the determination of cellulose. We have found that chlorine, when substituted for sulphuric acid in a high pressure cook with sawdust, gave a very fair yield of soluble and fermentable material, from which it might be concluded that the sugars were formed from the lignin portion of the wood. The following data, however, indicates that under the cooking conditions used the chlorine will attack pure cellulose, converting it into fermentable sugar. In these experiments, 0.2% chlorine, in the form of chlorine water, was used. The cooking method was in other respects similar to that already described.

TABLE NO. 2  
CHLORINE AS HYDROLYZING AGENT

| Material           | Total<br>Extract | Reducing<br>Substances | Fermentable<br>Sugars | Ratio Fer. Sug.<br>Total Ext. |
|--------------------|------------------|------------------------|-----------------------|-------------------------------|
| Sawdust            | 26.7             | 18.4                   |                       |                               |
| Sulphite Wood Pulp | 13.5             | 10.7                   | 8.0                   | .59                           |

Since the almost pure cellulose yields fermentable sugars, but in lesser amount than the ligno cellulose material, it would appear that both the cellulose and the lignin can be converted into sugar, at least with this special reagent.

The most conclusive data bearing on the question as to whether the cellulose or lignin portions of the wood yield sugar on hydrolysis is furnished by a series of experiments in which the change in the composition of the wood on cooking with acid has been determined. The cellulose in the original sawdust, in the residue from the first cook and in the residue from the re-cook, was determined by the Dean and Tower<sup>1</sup> modification of the Cross and Bevan method. The results of the cooks and analyses are given in Table No. 3.

If in the first cook the lignin alone had been attacked, the residue would have contained 70% of cellulose. If the cellulose alone had been attacked, the residue would have contained 41% of cellulose. After the second cook the sawdust residue was in finely divided physical condition and noticeably carbonized. A great deal of reliance cannot therefore be attached to the last cellulose determination. For similar reasons, it did not appear to be practicable to carry out cellulose determinations on the final residue.

This experiment indicates that the cellulose and the lignin go into solution, on high temperature hydrolysis, in about the same ration as they exist in the wood. Since the ratio of  $\frac{\text{Fermentable sugars}}{\text{Total extract}}$  is about the same for the wood extract as for the extracts from the pure celluloses, we conclude that both the cellulose and lignin can be equally converted into dextrose. The conversion of cellulose and wood by chlorine water is also in accord with this view.

Under the conditions of high temperature hydrolysis with dilute acid, the cellulose and the lignin do not react as chemical individuals, but rather as a chemical compound, ligno cellulose.

TABLE NO. 3

## EFFECT OF HYDROLYSIS ON CELLULOSE CONTENT OF WOOD

| Material                   | Total Extract | Reducing Material | Ferment. Sugars | Ratio Fer. Sug. Total Ext. | Cellulose Before Cooking | Cellulose After Cooking |
|----------------------------|---------------|-------------------|-----------------|----------------------------|--------------------------|-------------------------|
| a. Sawdust (Longleaf Pine) | 22.0%         | 19.3%             | 11.8%           | .53                        | 54.0%                    | 52.0%                   |
| b. Residue from (a)        | 6.3%          | 4.7%              | 3.0%            | .47                        | 52.0%                    | 42.0%                   |
| c. Residue from (b)        | 2.8%          | 1.7%              | 1.6%            | .57                        |                          |                         |

<sup>1</sup>J. A. C. S. 29 1119.



# DISTILLATION OF RESINOUS WOOD BY SATURATED STEAM

BY L. F. HAWLEY AND R. C. PALMER

*Forest Products Laboratory*

*Madison, Wisconsin*

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## INTRODUCTION. COMMERCIAL STEAM DISTILLATION PROCESSES

The steam distillation process for obtaining the volatile oils from the wood of the longleaf pine has been the basis of a small industry since about 1903, being introduced apparently in an attempt to produce wood turpentine at temperatures lower than those used in the destructive distillation processes then in operation, and thus to obtain a product uncontaminated by the decomposition products of wood and rosin. Quite a large number of plants have been built to use either sawmill waste or lightwood, or both, but many have been abandoned, probably only 12 or 15 being in operation in 1911. The quality of the crude turpentine produced has usually been very good, but because this is the only product obtained, or because the yield of this product is often lower than that of "crude turpentine" from other processes, the plants have been successful only under especially favorable conditions.

This process seems to be very promising, however, when combined with other processes for the utilization of the steamed chips, as for instance the extraction of the chips with volatile solvents for the removal of the rosin. Conditions are also favorable for this process in cases where the material would be largely used as fuel or wasted, or is very cheap or so poor in quality that more complicated processes would not be profitable; these conditions are commonly realized in the case of that part of the waste wood of sawmills now used as fuel at the plant or burned on the rubbish pile.

## PURPOSE OF INVESTIGATION

In the fields mentioned above the steam distillation of resinous woods will undoubtedly expand and it was in the hope of promoting this expansion and thus increasing the utilization of a class of material now wasted that this investigation on the fundamentals of the process was undertaken. There has been no uniformity in commercial practice or in the opinions of the various operators and no experimental data have been published on the effects produced by the different readily controlled variables, such as steam pressure, size of chips, or rapidity of distillation. In the methods described in various patent specifications the greatest stress has been laid on the mechanical features of charging and discharging, and of distributing the steam throughout the retort, which, although of great importance in the economy of a commercial method, throw no light on other equally important factors.

There seemed to be, therefore, a profitable field for investigation in determining the relations between the conditions under which the distillation is conducted on one hand and on the other hand the amount and kind of products and the readiness with which they are obtained.

## THEORETICAL CONSIDERATIONS

In the description of the experimental work and the discussion of the results it will be necessary to refer constantly to certain theoretical principles which apply to the distillation of volatile oils with steam, and in order to make the future discussions clearer, a brief presentation of these principles is given at this time.

In order to simplify the deductions the following assumptions are made in regard to the resinous material contained in the "lightwood" from the longleaf pine:<sup>1</sup>

<sup>1</sup>M. Vezes (Bull. Soc. Chem. 29, 470-478, 1903) has given a very clear and complete discussion of the principles underlying the distillation of the oleoresin from the Maritime pine of France. For the simplification of the discussion the following assumptions were made:

1. That the oleoresin is composed only of essence (turpentine) and colophony (rosin);
2. That these components are both simple substances completely soluble in each other;
3. That neither is soluble in water; and



1. It is composed only of turpentine, pine oil,<sup>2</sup> and rosin;
2. The components are all simple substances completely soluble in one another;
3. None of the components are soluble in water;
4. The turpentine and pine oil are both volatile, but the turpentine has the lower boiling point;
5. Rosin is nonvolatile.

While these assumptions are not strictly true in all cases, none of them are sufficiently incorrect to affect seriously the conclusions.

Concerning the distillation with steam of the resinous material defined by the above assumptions the following deductions can be made:

1. There will be a separation of the two volatile constituents, the turpentine being in greater proportion in the first part of the distillate and the pine oil in the latter part;
2. The temperature of the distillation under normal pressure will be slightly above 95° C. at the beginning, and will rise throughout the distillation, never quite reaching 100° C., however, as long as any of the turpentine or pine oil remains undistilled;
3. If the pressure at which the distillation is carried on is increased the temperature will be increased, the temperature depending upon the pressure and on the concentrations of the turpentine, pine oil, and rosin; the temperature will, however, never reach the steam temperature corresponding to the pressures used as long as any turpentine or pine oil remains undistilled.
4. The proportion of water to oil in the distillate will increase as the distillation progressed, this proportion being influenced

4. That rosin is nonvolatile.

In regard to the oleoresin obtained by chipping the live longleaf pine tree of the United States, the same assumption can be made, but the oleoresin contained in the pitchy "lightwood" from this species has another component, the heavy, high-boiling "pine oil" which must be taken into consideration in the discussion of the steam distillation of such wood.

<sup>2</sup>A discussion of the occurrence of pine oil in the "lightwood" of longleaf pine is given in Forest Service Bulletin 105 ("Wood Turpentines, their Analysis, Refining and Composition," by L. F. Hawley).

only by the relative amounts of the different constituents present in the oleoresin being distilled.<sup>1</sup>

In these deductions it is considered that the system is in complete equilibrium and under such conditions the behavior of this oleoresin when distilled with steam could be foretold with considerable accuracy, but in the distillation of wood containing the oleoresin there is a disturbing factor introduced which makes necessary the investigation of the variables mentioned in the introduction. This disturbing factor is the difficulty of keeping a complete equilibrium between the oleoresin and the steam, due to the fact that the wood surrounds the oleoresin and tends to keep the steam from coming in contact with it.

The effects of the size of chips and the rapidity of distillation are not due to a change of the laws governing the distillation of the oleoresin with steam, but to the manner in which they affect the completeness of the equilibrium in the system, or in other words, the completeness of contact between the oleoresin and the steam. In the same way the effects (other than temperature changes) of steam pressure on the results of the distillation are also due to its influence on the completeness of contact between steam and oleoresin rather than to any influence on the behavior of the steam and oleoresin when completely in equilibrium.

#### EXPERIMENTAL METHODS. APPARATUS AND MATERIALS

The vertical cylindrical retort used for the distillations was three feet long by fifteen inches in diameter, with removable heads, the bottom head carrying a steam jet and the top head an outlet valve. A pressure gauge was inserted in the body of the retort. An ordinary worm condenser was used and the distillate was caught in one-liter graduated cylinders.

The general plan of the work was to distill charges of the same sized chips under different conditions or of different sized chips under the same conditions, noticing carefully the differences in the results of the distillations. It was not practicable to make

<sup>1</sup>A change in the pressure at which the distillation is carried on might change the proportion of water to oil in the distillate but this change would be only slight and there is not sufficient data available to decide even the direction of this change.

all the runs on comparable material on account of the difficulty in preparing a large number of charges of the same resin content and also on account of the difficulty of keeping the prepared material without loss of volatile oil by evaporation. The runs were therefore made in groups, all of the material used in each group being comparable. All the charges were prepared from a single log of pitchy longleaf pine in which the pitch was distributed with unusual regularity.

#### DISTILLATION

Only a general description of the procedure will be given here; the same general methods were used in all cases and the details are given later in the tabulated record of the runs.

#### *Data Obtained*

A typical data sheet giving an example of the records obtained in each distillation is shown in Table 1. The distillate was caught in one-liter fractions and the time and pressure were recorded with every fraction. The amount of oil in each liter of distillate was determined as accurately as possible while in the original receiver (one-liter cylinders graduated to 10 cc.); the oil was then separated from the water in a separatory funnel and its specific gravity determined. When the amount of oil in the fractions was so small that a specific gravity determination could not readily be made on a single fraction the oil from a sufficient number of fractions was combined to make the determination possible. As a check on the total amount of oil computed from the rough measurements on the separate fractions the combined oil from all the fractions or from the fractions of different portions of the distillation was accurately measured.

The detailed records for each distillation will not be given in this report, but instead the essential part of this data will be tabulated together with other factors computed from the data. The discussion of the data from all groups will be taken up together after the experimental work has been described.

TABLE 1.—TYPICAL DATA SHEET, ILLUSTRATING THE RECORDS TAKEN OF THE DISTILLATIONS

PROJECT 123—RUN No. 23

CHIPS 1" x 2" x 2"

Weight of can + water— 160 lbs.  
 Weight of can + water + chips— 215 lbs. Steam turned on— 9.23  
 Weight of chips— 55 lbs. Distillate began to flow—9.28.30

| TIME |      | Liters<br>of<br>Distillate | cc. of Oil<br>in<br>Distillate | cc. of Oil<br>Total<br>Com-<br>puted | cc. of Oil<br>To'al<br>Determined | Specific<br>Gravity<br>of Oil | Pressure |
|------|------|----------------------------|--------------------------------|--------------------------------------|-----------------------------------|-------------------------------|----------|
| Hrs. | Min. |                            |                                |                                      |                                   |                               |          |
| 9    | 36   | 1                          | 88                             | 88                                   | 362                               | .8810                         | 70       |
| 9    | 48   | 2                          | 154                            | 242                                  |                                   | .8794                         | 72       |
| 9    | 59½  | 3                          | 110                            | 352                                  |                                   | .8851                         | 71       |
| 10   | 8    | 4                          | 73                             | 425                                  |                                   | .8944                         | 71       |
| 10   | 17   | 5                          | 60                             | 485                                  |                                   |                               | 68       |
| 10   | 29½  | 6                          | 55                             | 540                                  |                                   | .8980                         | 71       |
| 10   | 40½  | 7                          | 50                             | 590                                  |                                   |                               | 70       |
| 10   | 51½  | 8                          | 44                             | 634                                  |                                   | .8981                         | 72       |
| 11   | ½    | 9                          | 39                             | 673                                  |                                   |                               | 70       |
| 11   | 8½   | 10                         | 24                             | 697                                  |                                   | .9010                         | 69       |
| 11   | 18½  | 11                         | 27                             | 724                                  | 839                               |                               | 72       |
| 11   | 28   | 12                         | 26                             | 750                                  |                                   |                               | 69       |
| 11   | 38   | 13                         | 19                             | 769                                  |                                   |                               | 72       |
| 11   | 47½  | 14                         | 22                             | 791                                  |                                   | .9016                         | 68       |
| 11   | 57½  | 15                         | 17                             | 808                                  |                                   |                               | 69       |
| 12   | 7    | 16                         | 17                             | 825                                  |                                   |                               | 69       |
| 12   | 17   | 17                         | 16                             | 841                                  |                                   |                               | 69       |
| 12   | 27½  | 18                         | 16                             | 857                                  |                                   | .8987                         | 72       |
| 12   | 38½  | 19                         | 18                             | 875                                  |                                   |                               | 72       |
| 12   | 50   | 20                         | 19                             | 894                                  |                                   |                               | 64       |
| 1    | 0    | 21                         | 15                             | 909                                  | 979                               |                               | 71       |
| 1    | 9    | 22                         | 13                             | 922                                  |                                   | .8965                         | 72       |
| 1    | 18½  | 23                         | 11                             | 933                                  |                                   |                               | 71       |
| 1    | 27½  | 24                         | 10                             | 943                                  |                                   |                               | 69       |
| 1    | 39   | 25                         | 12                             | 955                                  |                                   |                               | 68       |
| 1    | 48   | 26                         | 10                             | 965                                  |                                   |                               | 70       |
| 2    | 0    | 27                         | 11                             | 976                                  |                                   |                               | 70       |
| 2    | 11½  | 28                         | 10                             | 986                                  |                                   |                               | 68       |
| 2    | 23½  | 29                         | 12                             | 998                                  |                                   | .8958                         | 72       |
| 2    | 34½  | 30                         | 8                              | 1006                                 |                                   |                               | 73       |
| 2    | 45½  | 31                         | 8                              | 1016                                 | 1047                              |                               | 72       |
| 2    | 56½  | 32                         | 10                             | 1026                                 |                                   |                               | 63       |
| 3    | 7½   | 33                         | 13                             | 1039                                 |                                   |                               | 45       |
| 3    | 17   | 34                         | 6                              | 1045                                 |                                   |                               | 32       |
| 3    | 26½  | 35                         | 5                              | 1050                                 |                                   |                               | 20       |
| 3    | 37   | 36                         | 4                              | 1054                                 |                                   | .8936                         | 12       |
| 3    | 43   | 37                         | 1                              | 1055                                 |                                   |                               | 4        |
| 3    | 45   | 38                         | 1                              | 1056                                 | 1095                              |                               | 0        |



TABLE 1.—*Continued.*

| TIME                                |      | Liters<br>of<br>Distillate | cc. of Oil<br>in<br>Distillate | cc. of Oil<br>Total<br>Com-<br>puted | cc. of Oil<br>Total<br>Determined | Specific<br>Gravity<br>of Oil | Pressure |
|-------------------------------------|------|----------------------------|--------------------------------|--------------------------------------|-----------------------------------|-------------------------------|----------|
| Hrs.                                | Min. |                            |                                |                                      |                                   |                               |          |
| Distillation interrupted over night |      |                            |                                |                                      |                                   |                               |          |
| 9                                   | 23½  | 39                         | 22                             | 1078                                 | }                                 | .8934                         | 72       |
| 9                                   | 35   | 40                         | 17                             | 1095                                 |                                   |                               | 73       |
| 9                                   | 46   | 41                         | 15                             | 1110                                 |                                   |                               | 71       |
| 9                                   | 57   | 42                         | 10                             | 1120                                 |                                   |                               | 72       |
| 10                                  | 8    | 43                         | 9                              | 1129                                 | }                                 | .9003                         | 70       |
| 10                                  | 19   | 44                         | 8                              | 1137                                 |                                   |                               | 72       |
| 10                                  | 30   | 45                         | 7                              | 1143                                 |                                   |                               | 58       |
| 10                                  | 43   | 46                         | 15                             | 1158                                 |                                   |                               | 34       |
| 10                                  | 53   | 47                         | 8                              | 1166                                 | }                                 | .8935                         | 19       |
| 11                                  | 4    | 48                         | 6                              | 1172                                 |                                   |                               | 6        |
| 11                                  | 6    | 49                         | 2                              | 1174                                 | 1235                              |                               | 0        |

| No. of Liters | Yield cc. lb. | Efficiency |
|---------------|---------------|------------|
| 16            | 15.3          | .95        |
| 25            | 17.8          | .71        |
| 38            | 19.9          | .51        |
| 49            | 22.4          | .46        |

*End Point*

It will be noticed in Table 1 that the amount of oil in one liter of distillate gradually decreased and decreased very slowly toward the end of a distillation. On this account it became necessary to arbitrarily choose a ratio of oil to water which might be considered as the end of a distillation under one set of conditions in order to make the results of different distillations comparable and at the same time to keep the time required within practicable limits. In the first five runs the end point was too high and too variable, since it was not recognized that the end point must be very carefully regulated in order to obtain comparable results. These first five runs are, therefore, not comparable with those which follow in which the end point was carefully regulated at somewhat lower values. It was also found that after distilling a charge under one set of conditions until a certain end point was reached, if the distillation was interrupted for an hour or more and



TABLE II.—SUMMARY RECORD OF EXPERIMENTAL RUNS

| GROUP<br>No. | RUN<br>No. | SIZE OF CHIPS    | 0 LBS. PRESSURE      |                 | 20 AND 30 LBS.<br>PRESSURE |                 | 40 AND 50 LBS.<br>PRESSURE |                 | 70 LBS.<br>PRESSURE  |                 | TOTAL                |                 | SPEED<br>MIN.<br>PER<br>LITER | END<br>POINT<br>CC. PER<br>LITER |
|--------------|------------|------------------|----------------------|-----------------|----------------------------|-----------------|----------------------------|-----------------|----------------------|-----------------|----------------------|-----------------|-------------------------------|----------------------------------|
|              |            |                  | Yield cc.<br>per lb. | Effi-<br>ciency | Yield cc.<br>per lb.       | Effi-<br>ciency | Yield cc.<br>per lb.       | Effi-<br>ciency | Yield cc.<br>per lb. | Effi-<br>ciency | Yield cc.<br>per lb. | Effi-<br>ciency |                               |                                  |
| I            | 1          | Sawdust          | 20.6                 | 1.71            | .....                      | ...             | 9.9 <sup>c</sup>           | .45             | ....                 | ...             | 30.5                 | .90             | 4                             | 25 and 12                        |
|              | 2          | Sawdust          | .....                | .....           | .....                      | ...             | 32.7 <sup>c</sup>          | 1.26            | ....                 | ...             | 32.7                 | 1.26            | 4                             | 18                               |
|              | 3          | Sawdust          | 12.5                 | 1.56            | .....                      | ...             | 8.2 <sup>c</sup>           | .41             | ....                 | ...             | 20.7                 | .74             | 4                             | 17 and 12                        |
|              | 4          | 2" x 1" x 1"     | .....                | .....           | .....                      | ...             | .....                      | .....           | 20.3                 | .33             | 20.3                 | .33             | 5                             | 12                               |
|              | 5          | 2" x 1" x 1"     | 6.4                  | .61             | 5.8 <sup>a</sup>           | .45             | 3.9 <sup>c</sup>           | .33             | 9.1                  | .33             | 25.2                 | .38             | 4                             | 12                               |
|              | 6          | 2" x 1" x 1"     | 8.0                  | .55             | 5.1 <sup>a</sup>           | .28             | 6.1 <sup>c</sup>           | .24             | .....                | ...             | 19.2                 | .34             | 10                            | 10                               |
|              | 7          | 1" x 1" x 1"     | 15.7                 | .63             | 4.6 <sup>a</sup>           | .29             | 5.3 <sup>c</sup>           | .24             | .....                | ...             | 25.6                 | .40             | 10                            | 10                               |
|              | 8          | 1" x 1" x 1"     | 10.2                 | .46             | 6.5 <sup>a</sup>           | .25             | 6.2 <sup>c</sup>           | .19             | .....                | ...             | 23.0                 | .29             | 10                            | 10                               |
|              | 9          | 1" x 2" x 1"     | .....                | .....           | 22.4 <sup>b</sup>          | .46             | 3.0 <sup>d</sup>           | .19             | 4.5                  | .21             | 29.9                 | .34             | 10                            | 10                               |
|              | 10         | 1" x 2" x 1"     | .....                | .....           | .....                      | ...             | 27.2 <sup>d</sup>          | .46             | 1.5                  | .12             | 28.7                 | .40             | 10                            | 10                               |
| II           | 11         | Sawdust          | 27.7                 | 1.46            | .....                      | ...             | 2.0 <sup>c</sup>           | .25             | .....                | ...             | 29.7                 | 1.1             | 10                            | 10                               |
|              | 12         | 1" x variable    | .....                | .....           | .....                      | ...             | .....                      | .....           | 25.7                 | .49             | 25.7                 | .49             | 10                            | 10                               |
|              | 13         | 6" x variable    | .....                | .....           | .....                      | ...             | .....                      | .....           | 12.3                 | .29             | 12.3                 | .29             | 10                            | 10                               |
| III          | 14         | 1" x 5" x 8"     | .....                | .....           | .....                      | ...             | 19.7 <sup>d</sup>          | .35             | 5.9                  | .17             | 25.6                 | .28             | 10                            | 10                               |
|              | 15         | 1" x 3" x 1 1/2" | .....                | .....           | .....                      | ...             | 24.5 <sup>d</sup>          | .41             | 4.7                  | .15             | 29.2                 | .32             | 10                            | 10                               |
| IV           | 16         | Sawdust          | 25.2                 | .97             | .....                      | ...             | 4.0 <sup>c</sup>           | .31             | .....                | ...             | 29.1                 | .75             | 10                            | 10                               |
|              | 17         | 1" x 1" x 1"     | .....                | .....           | 24.5 <sup>b</sup>          | .50             | .....                      | .....           | .....                | ...             | .....                | .....           | 10                            | 10                               |
|              | 18         | 1" x 1" x 1"     | .....                | .....           | .....                      | ...             | 26.8 <sup>d</sup>          | .50             | .....                | ...             | .....                | .....           | 10                            | 10                               |
|              | 19         | 1" x 3" x 1 1/2" | .....                | .....           | .....                      | ...             | 25.3 <sup>d</sup>          | .55             | .....                | ...             | .....                | .....           | 10                            | 10                               |
|              | 20         | 1" x 3" x 1 1/2" | .....                | .....           | .....                      | ...             | .....                      | .....           | 29.8                 | .63             | 29.8                 | .63             | 10                            | 10                               |
| V            | 21         | Sawdust          | 24.6                 | 1.05            | .....                      | ...             | 1.7 <sup>c</sup>           | .23             | .....                | ...             | 26.3                 | .82             | 10                            | 10                               |
|              | 22         | 1" x 2" x 2"     | .....                | .....           | .....                      | ...             | .....                      | .....           | 23.1                 | .39             | 23.1                 | .39             | 10                            | 10                               |
|              | 23         | 1" x 2" x 2"     | .....                | .....           | .....                      | ...             | .....                      | .....           | 22.4                 | .46             | 22.4                 | .46             | 10                            | 10                               |

a = 20 lbs.

b = 30 lbs.

c = 40 lbs.

d = 50 lbs.

TABLE II.—SUMMARY RECORD OF EXPERIMENTAL RUNS—Continued

| GROUP No. | RUN No. | SIZE OF CHIPS | 0 LBS. PRESSURE   |            | 20 AND 30 LBS. PRESSURE |            | 40 AND 50 LBS. PRESSURE |            | 70 LBS. PRESSURE  |            | TOTAL             |            | SPEED MIN. PER LITER | END POINT cc. PER LITER |
|-----------|---------|---------------|-------------------|------------|-------------------------|------------|-------------------------|------------|-------------------|------------|-------------------|------------|----------------------|-------------------------|
|           |         |               | Yield cc. per lb. | Efficiency | Yield cc. per lb.       | Efficiency | Yield cc. per lb.       | Efficiency | Yield cc. per lb. | Efficiency | Yield cc. per lb. | Efficiency |                      |                         |
| VI        | 24      | 1" x 4" x 4"  | ....              | ...        | ....                    | ...        | ....                    | ...        | 23.6              | .44        | 23.8              | .44        | 10                   | 10                      |
|           | 25      | Sawdust       | 24.0              | .89        | ....                    | ...        | 2.6°                    | .26        | 23.6              | .44        | 23.6              | .70        | 10                   | 10                      |
|           | 26      | 1" x 1" x 1"  | ....              | ...        | ....                    | ...        | ....                    | ...        | 22.8              | .45        | 22.8              | .45        | 10                   | 10                      |
|           | 27      | 2" x 1" x 1"  | ....              | ...        | ....                    | ...        | ....                    | ...        | 21.4              | .31        | 21.4              | .31        | 10                   | 10                      |
|           | 28      | 3" x 1" x 1"  | ....              | ...        | ....                    | ...        | ....                    | ...        | 12.9              | .29        | 12.9              | .29        | 10                   | 10                      |
| VII       | 29      | Sawdust       | 19.3              | .84        | ....                    | ...        | 1.7°                    | .17        | ....              | ...        | 21.0              | .64        | 10                   | 10                      |
|           | 30      | Shavings      | 18.8              | .94        | ....                    | ...        | ....                    | ...        | ....              | ...        | ....              | ...        | 6                    | 5                       |
|           |         |               | .6                | ...        | ....                    | ...        | ....                    | ...        | ....              | ...        | ....              | ...        | 10                   | 7                       |
|           |         |               | 19.4              | .85        | ....                    | ...        | ....                    | ...        | ....              | ...        | ....              | ...        | 6 and 10             | 5 and 7                 |
|           |         |               | ....              | ...        | ....                    | ...        | 3.1°                    | .39        | ....              | ...        | 22.5              | .73        | 10                   | 10                      |
|           |         |               | ....              | ...        | ....                    | ...        | ....                    | ...        | ....              | ...        | ....              | ...        | 6 and 10             | 5 and 7                 |
|           | 31      | Shavings      | 16.0              | .84        | ....                    | ...        | ....                    | ...        | ....              | ...        | ....              | ...        | 3                    | 5                       |
|           |         |               | 1.4               | ...        | ....                    | ...        | ....                    | ...        | ....              | ...        | ....              | ...        | 10                   | 7                       |
|           |         |               | 17.4              | .70        | ....                    | ...        | ....                    | ...        | ....              | ...        | ....              | ...        | 3 and 10             | 5 and 7                 |
|           |         |               | ....              | ...        | ....                    | ...        | 3.8°                    | .38        | ....              | ...        | ....              | ...        | 10                   | 10                      |
| 32        |         | 1" x 1" x 1"  | ....              | ...        | ....                    | ...        | ....                    | ...        | ....              | ...        | 21.2              | .60        | 3 and 10             | 5 and 7                 |
|           |         |               | ....              | ...        | ....                    | ...        | ....                    | ...        | 20.1              | .43        | ....              | ...        | 6                    | 5                       |
|           |         |               | ....              | ...        | ....                    | ...        | ....                    | ...        | .7                | ...        | ....              | ...        | 10                   | 7                       |
| 33        |         | 1" x 1" x 1"  | ....              | ...        | ....                    | ...        | ....                    | ...        | 20.8              | .39        | 20.8              | .39        | 6 and 10             | 5 and 7                 |
|           |         |               | ....              | ...        | ....                    | ...        | ....                    | ...        | 18.1              | .39        | ....              | ...        | 3                    | 5                       |
|           |         |               | ....              | ...        | ....                    | ...        | ....                    | ...        | 2.2               | ...        | ....              | ...        | 10                   | 7                       |
|           |         |               | ....              | ...        | ....                    | ...        | ....                    | ...        | 20.3              | .33        | 20.3              | .33        | 3 and 10             | 5 and 7                 |

d = 50 lbs.

c = 40 lbs.

b = 30 lbs.

a = 20 lbs.

then continued under the same conditions as before, a further supply of oil could be obtained before the same end point was reached again. This additional amount of oil obtained as a result of interrupting the distillation amounted to from 2 per cent to 18.8 per cent of the oil already obtained before the distillation was interrupted. The highest increases in yields due to this manipulation were those runs where there was still considerable oil present in the wood when the distillation was interrupted (although, of course, all the oil possible had been removed under the prevailing conditions). For instance, in Runs 14 and 15, after all the oil possible had been distilled at 50-pounds pressure, interruption of the distillations over night made it possible to distill respectively 18.8 per cent and 15.1 per cent more oil under the same conditions; in both these cases there was still considerable oil present in the wood as shown by further distillation at increased pressures. In Runs 11 and 21, however, after all the oil possible had been distilled at atmospheric pressure, interruption of the distillations made it possible to obtain only 2.9 per cent and 4.0 per cent more oil under the same conditions; in these cases there were much smaller quantities of oil left in the wood than in Runs 14 and 15.

This effect also was not recognized as important until after Run 5 was finished, so that for another reason Runs 1 to 5 are not comparable with those which follow.

The proper end point for any distillation after Run 5 was considered to be reached only when the required ratio of oil to water in the distillate had been attained both before and after interruption of the distillation.

#### DISCUSSION OF RESULTS

The data obtained by the distillation of the various runs are given in Table 2 together with the conditions under which the distillations were made. In the table the size of the chip as given in column two is expressed in inches with the length parallel to the grain given first. The values given in the columns headed "Yield" are expressed in cc. of oil per pound of wood. The possible error in these determinations of yields is apparently about 6 to 7 per cent and is due to difficulties in sampling, in regulating

evaporation during the preparation of material, and in obtaining comparable end points in different distillations.

An example of results which must be due to such errors is seen in Runs 23 and 24. The chips in Run 24 are larger than those in Run 23 and the yield should be perhaps less and certainly not greater from the larger chips, and yet the yields obtained from Run 23 are 5.0 per cent less than those from Run 24. Another similar example is shown in Runs 30 and 31. It might be thought that some of these variations in yields were due to incomplete distillation caused by the "channeling" of the steam through the charge in such a way that part of the wood was never touched by the steam, but in several runs after all the oil possible had been distilled under some one set of conditions the top of the retort was removed, the charge well stirred, and the distillation continued under the same conditions as before without any indications that the stirring had discovered undistilled material in the charge. It seems probable, therefore, that with a retort of the shape and size used in these distillations the effect of incomplete distillation due to incomplete contact between the steam and the surface of the chips is negligible.

TABLE 3.—EFFECT OF SIZE OF CHIP ON YIELD AND EFFICIENCY

| Run No.        | Size of Chip   | Pressures   | Yields                   | Efficiency            | Speed Min. Per Liter | End Point cc. Oil Per Liter Distillate |
|----------------|--|-------------|--------------------------|-----------------------|----------------------|--|
| 7<br>8         | $1'' \times \frac{1}{4}'' \times \frac{1}{8}''$ }<br>$1'' \times \frac{1}{2}'' \times \frac{1}{4}''$ } | atmospheric | { 15.7<br>10.2 }         | { .63<br>.46 }        | 10                   | 10                                     |
| 12<br>13       | $1''$ sections from slabs }<br>$6''$ sections from same }  | 70 pounds   | { 25.7<br>12.3 }         | { .49<br>.29 }        | 10                   | 10                                     |
| 14<br>15       | $1'' \times 5'' \times 8''$ }<br>$1'' \times 1\frac{1}{2}'' \times 1\frac{1}{2}''$ }                   | 50 pounds   | { 19.7<br>24.5 }         | { .35<br>.41 }        | 10                   | 10                                     |
| 26<br>27<br>28 | $1'' \times 1'' \times 1''$ }<br>$2'' \times 1'' \times 1''$ }<br>$3'' \times 1'' \times 1''$ }        | 70 pounds   | { 22.8<br>21.4<br>12.9 } | { .45<br>.31<br>.29 } | 10                   | 10                                     |

The values given under "Efficiency" are obtained by dividing the yields per pound of wood by the number of liters of total distillate, the efficiency factor being cc. oil per pound of wood

TABLE 4.—EFFECT OF PRESSURE ON YIELD AND EFFICIENCY

| Run No. | Size of Chip                           | Pressures   | Yields | Efficiency | Speed Min. Per Liter | End Point cc. Oil Per Liter Distillate |
|---------|--|-------------|--------|------------|----------------------|--|
| 8       | 1" x $\frac{1}{2}$ " x $\frac{1}{4}$ " | Atmospheric | 10.2   | .46        | 10                   | 10                                     |
| 9       | 1" x $\frac{1}{2}$ " x $\frac{1}{4}$ " | 30 pounds   | 22.4   | .46        | 10                   | 10                                     |
| 10      | 1" x $\frac{1}{2}$ " x $\frac{1}{4}$ " | 50 pounds   | 27.2   | .46        | 10                   | 10                                     |
| 17      | 1" x $\frac{1}{4}$ " x $\frac{1}{8}$ " | 30 pounds   | 24.5   | .50        | 10                   | 10                                     |
| 18      | 1" x $\frac{1}{4}$ " x $\frac{1}{8}$ " | 50 pounds   | 26.8   | .50        | 10                   | 10                                     |
| 19      | 1" x $\frac{1}{2}$ " x $\frac{1}{2}$ " | 50 pounds   | 25.3   | .55        | 10                   | 10                                     |
| 20      | 1" x $\frac{1}{2}$ " x $\frac{1}{2}$ " | 70 pounds   | 29.8   | .63        | 10                   | 10                                     |

per liter of distillate or  $\frac{\text{cc. oil}}{\text{pounds wood} \times \text{liters distillate}}$ . It might be thought that this "efficiency factor" would have more significance if it represented only the relation between oil and total distillate, but, as will be seen later,<sup>1</sup> this relation would be affected by the amount of wood distilled. Of course, the effect may not be in exact proportion to the amount of wood distilled as represented in the factor used, but it is thought that more nearly comparable efficiency factors are obtained by including the amount of wood as above. These factors represent approximately the relative amounts of oil obtained in the different runs per unit of steam consumed, exclusive of the steam which supplies the heat lost by radiation.

#### EFFECT OF SIZE OF CHIP ON YIELD AND EFFICIENCY

In general, other conditions being the same, the smaller the chip, the larger the yields and the higher the efficiency. This is shown in Table 3 which contains selected data from Table 2. Four groups of distillations are given, in each of which all the other conditions except size of chip are as nearly as possible the same, and in every case the smaller-sized chips show the larger yield and higher efficiency. The effect on yield is not so marked in the case of Runs 26 and 27 (and some of the other runs given in Table 2) but this is accounted for by the fact that the pressure was high enough so that nearly all the oil was removed even from

<sup>1</sup>The same reasoning as is given on page 168 regarding the effect of the size of retort on the efficiency applies also to the effect of the amount of wood distilled on the efficiency.



the larger-sized chips. In the case of two runs in which all the oil was removed even from the larger chips the yields would of course be the same, but the efficiency would probably be higher with the smaller-sized chips.

#### EFFECT OF PRESSURE ON YIELD AND EFFICIENCY

In general, other conditions being the same, higher pressures give larger yields without lowering the efficiency. This is shown in Table 4 which gives three groups of runs, in each of which all conditions except steam pressure are as nearly as possible the same. In all cases the higher steam pressure produced the larger yield and with the same or higher efficiency. The effect of pressure on yields is also shown in another way in many of the runs in Table 2 in which after obtaining all the oil possible by distilling under one pressure a further yield of oil was obtained by continuing the distillation under a higher pressure.

#### EFFECT OF SPEED OF DISTILLATION ON YIELDS AND EFFICIENCY

Other conditions being the same, increased speed of distillation decreases both the yield and the efficiency. This is shown clearly in Table 5 which gives the results of two sets of two runs each, all the conditions except the speed being the same in each set. The more rapid passage of the steam through the charge probably causes it to be less completely saturated with the oil vapors, thus directly decreasing the efficiency. The yield is decreased probably because the same end point is reached sooner when the steam is less completely saturated. This is indicated by the more nearly equal total yields obtained in each set of runs by finishing up the distillations at the same pressure but at lower speeds. The variation in efficiency is not, however, as might be expected, exactly proportional to the speed, since doubling the speed decreases the efficiency by only about 10 per cent, from .94 to .84 in Runs 30 and 31, and from .43 to .39 in Runs 32 and 33.

If, as seems probable, the effects of speed are due to the variations in the time during which the steam is in contact with the

wood, then the size of the retort would have a similar effect; that is, a speed of 10 minutes per liter in a certain sized retort would be equivalent to 5 minutes per liter in a retort twice as large, since a unit of steam would be in contact with a unit of wood for the same length of time in either case.

TABLE 5.—EFFECT OF SPEED ON YIELD AND EFFICIENCY

| Run No. | Size of Material | Pressure                   | Speed Min. Per Liter | End point cc. Oil per Liter | Yield | Total Yield | Efficiency | Total Efficiency |
|---------|------------------|----------------------------|----------------------|-----------------------------|-------|-------------|------------|------------------|
| 30      | Shavings         | { Atmospheric<br>40 pounds | 6                    | 5                           | 18.8  | 18.8        | .94        | .94              |
|         |                  |                            | 10                   | 7                           | .6    | 19.4        | ...        | .85              |
|         |                  |                            | 10                   | 10                          | 3.1   | 22.5        | .39        | .73              |
| 31      | Shavings         | { Atmospheric<br>40 pounds | 3                    | 5                           | 16.0  | 16.0        | .84        | .84              |
|         |                  |                            | 10                   | 7                           | 1.4   | 17.4        | ...        | .70              |
|         |                  |                            | 10                   | 10                          | 3.8   | 21.2        | .38        | .60              |
| 32      | 1" x 1/2" x 1/2" | 70 pounds                  | { 6                  | 5                           | 20.1  | 20.1        | .43        | .43              |
|         |                  |                            | { 10                 | 7                           | .7    | 20.8        | ...        | .39              |
| 33      | 1" x 1/2" x 1/2" | 70 pounds                  | { 3                  | 5                           | 18.1  | 18.1        | .39        | .39              |
|         |                  |                            | { 10                 | 7                           | 2.2   | 20.3        | ...        | .33              |

## RELATIONS BETWEEN END POINT, YIELD AND EFFICIENCY

As shown in Table 1 the amount of oil in a liter of total distillate is greatest at the beginning of the distillation and decreases steadily as the distillation progresses, except when the conditions of distillation are changed, and then the increase in the amount of oil per liter is usually only slight and temporary. This was true in all the distillations and it is evident, therefore, that the efficiency factor will decrease steadily throughout the distillation and its final value will depend on the end point used. Therefore, the efficiency can be increased by stopping the distillation before all the oil possible has been obtained and thus decreasing the total yield of oil. For the same reason the efficiency will be decreased by continuing the distillation until all the oil possible has been obtained and thus increasing the total yield of oil. For instance, in Run No. 23 (Table 2) if the distillation had been stopped with an end point of 12 cc. per liter,

at the 25th liter the yield would have been only 15.3 cc. per pound while the efficiency would have been .95. By continuing the distillation until the end point (after an interruption of the distillation) was 10 cc. per liter, a much larger yield, 22.4 cc. per pound was obtained, but only at the expense of much decreased efficiency (.46).

THE PRESSURES REQUIRED TO DISTILL COMPLETELY  
DIFFERENT SIZES OF MATERIAL

*Sawdust*

The volatile oil cannot be completely distilled at atmospheric pressure even from a material as finely divided as sawdust. This can be seen from Runs 11, 16, 21, 25, and 29, in which, after removing all the oil possible at atmospheric pressure, a further distillation at 40 pounds pressure removed from 6.6 to 15.8 per cent more oil. It was found that after distilling at 40 pounds pressure a further distillation at 70 pounds was without appreciable effect. It can be safely stated that 40 pounds pressure is sufficient for the removal of all the volatile oil from material as small as sawdust. It is possible that lower pressures might give almost as good results but this point can not be determined from the data on hand.

*Chips  $1'' \times \frac{1}{4}'' \times \frac{1}{8}''$*

This size material cannot be completely distilled at 30 pounds pressure (Run 17) and probably not at 50 pounds pressure (Run 18). In Run 18 the yield obtained from chips  $1'' \times \frac{1}{4}'' \times \frac{1}{8}''$  is almost the same, within the limit of possible variation, as from the sawdust of Run 16, but apparently not quite all the oil has been removed.

*Chips  $1'' \times \frac{1}{2}'' \times \frac{1}{2}''$*

Chips of this size cannot be completely distilled at 50 pounds pressure (Run 19) but can at 70 pounds (Runs 20, 32, and 33).

*Chips larger than  $1'' \times \frac{1}{2}'' \times \frac{1}{2}''$*

At the maximum pressure used, 70 pounds, chips larger than  $1'' \times \frac{1}{2}'' \times \frac{1}{2}''$  cannot be completely distilled, but as the size of chips is increased there is no sudden drop in the yields obtainable at this pressure until sizes larger than 2 inches with the grain (Runs

27 and 28)<sup>1</sup> and 4 by 4 inches across the grain are used (Runs 14 and 24). It is probable that 80 to 85 per cent of the oil could be removed from chips 2"x4"x4" by distillation at 70 pounds pressure.

#### EFFECT OF PRESSURE ON COMPOSITION OF OIL

Analyses were made by the method described in Bulletin 105 of part or all of the oil from each of the runs, but there was not enough difference between the various samples so that all of the analyses will need to be given. A few distillation curves showing the main points of interest will be given.

#### *Pine Oil*

The proportion of pine oil in the crude turpentine did not vary except in cases which could be explained by variation in other factors besides pressure and, therefore, so far as the results show, the pressure has no influence on the proportion of pine oil except the influence due to increasing the total yields. In all cases where the total oil obtained was analyzed, and where the oil was nearly completely removed from the wood, the percentage of pine oil by weight varied only between 48 per cent and 52 per cent.<sup>2</sup> In cases where only part of the oil was removed by the distillation, as in Run 4, the proportion of pine oil was less.

<sup>1</sup>In determining the percentage of total oil obtained in the runs of Group VI it must be remembered that the sawdust of Run 25 was not exactly a representative sample of the material of that group but that it was mixed with the sawdust obtained in cutting the slabs from the blocks. In several cases similar samples of sawdust obtained in cutting the slabs had been distilled and found to contain more volatile oil than the sawdust obtained in cutting the blocks. It is probable, therefore, that the proportion of volatile oil in the mixed sample of sawdust was somewhat greater than in the rest of the material in this group. This point is further indicated by a comparison of the yields obtained from the sawdust runs in the different groups. With the exception of Group VI (Run 25) the yields from the sawdust decrease, as might be expected for the reason that the material for the groups was cut from the same log in order of the group number, beginning at the butt end and the content of volatile oil in the butt end was higher than in the upper portions of the log. It is probable, therefore, that a value of 24 to 25 cc. oil per pound of wood would more nearly represent the volatile oil content of the group.

<sup>2</sup>Exceptions were found to this in the oils from Group II which contained about 28 per cent pine oil. But the material for this group did not represent a complete cross section of the log, being composed instead only of the outside pieces, the slabs. The outer layers of this log evidently contained a smaller proportion of pine oil than the rest of the wood.



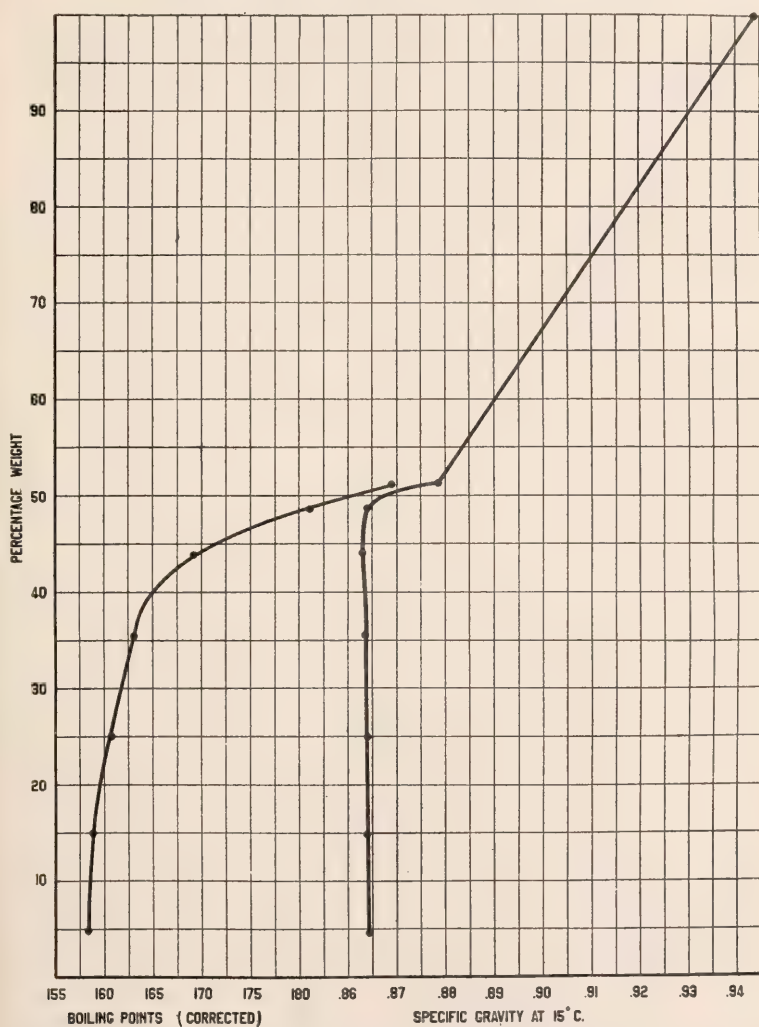


Figure 1. BOILING POINT AND SPECIFIC GRAVITY CURVES FOR OIL FROM RUN 21



### *Dipentene*

The detection of small differences in the proportion of dipentene present cannot be made by the method of examination used, especially when such large proportions of pine oil are present. There seemed to be, however, more dipentene in the crude turpentine produced at higher pressures. Figures 1 and 2, representing the distillation curves obtained in the analyses of the oils from Runs 21 and 23, respectively, illustrate this point. The oil obtained from sawdust mostly at atmospheric pressure (Figure 2) apparently contains less dipentene than the oil distilled entirely at 70 pounds pressure (Figure 2); the specific gravity values being lower and the proportion of the oil boiling between 165° and 180° larger in the latter case. It had formerly been thought that the dipentene which had been found in wood turpentine was caused by the temperature used in distilling the oil from the wood, but indications of dipentene were found in all the samples of oil obtained in this investigation, even in those produced at atmospheric pressure, and it is very probable that dipentene was present as such in the wood distilled. In order to make sure that this material with low specific gravity and high-boiling point was dipentene and not some other terpene with similar physical properties, a chemical examination was made of the fractions 165° to 185° from some of the turpentine produced at atmospheric pressure and dipentene was identified by means of the tetrabromide, M. P., 125°-126°.

In order to determine the possibility of the transformation of pinene into dipentene under the condition of steam distillation the sawdust from Run 29 was air dried and moistened with 1175 cc. of gum turpentine (an amount equal to the total volatile oil originally present) and distilled at atmospheric pressure. The oil on analysis showed no indications of dipentene. The experiment was repeated, making the distillation at 50 pounds pressure, but with the same result. These results preclude the possibility of formation of dipentene from pinene under the conditions of steam distillation pressures below 50 pounds and indicate very strongly that dipentene occurs as such in lightwood.

### *Light Oils*

Figures 1 and 2 also illustrate another effect of pressure on

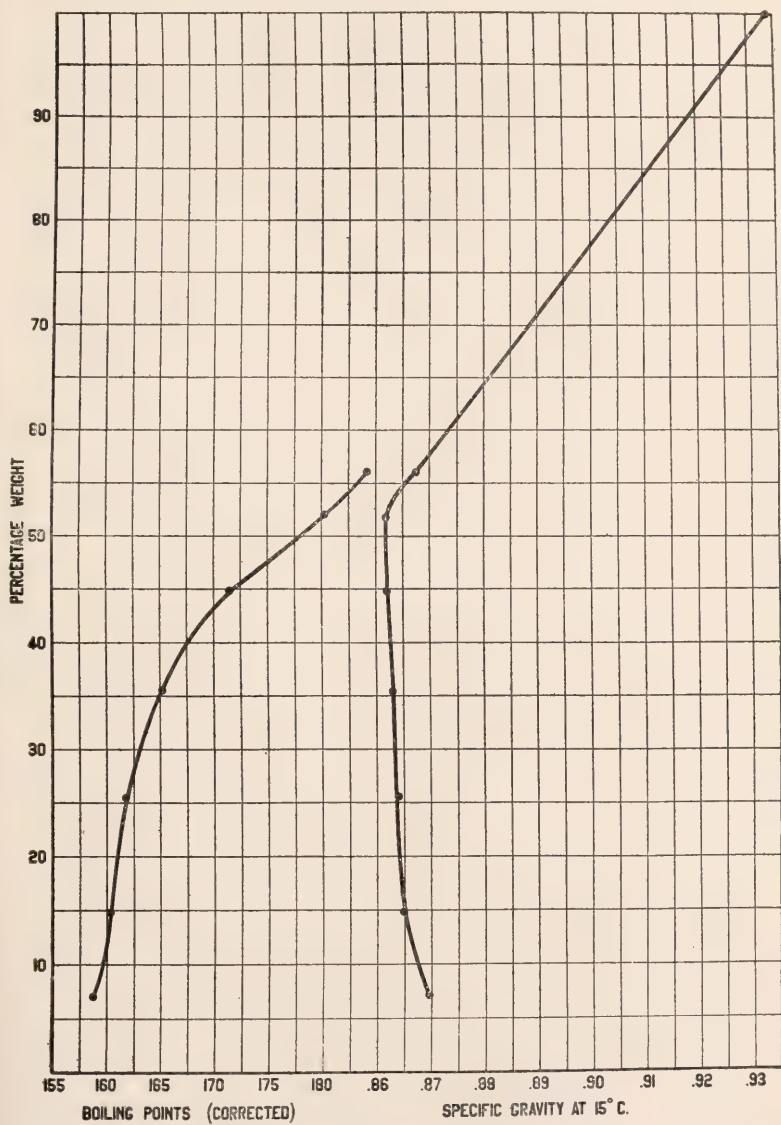


Figure 2. BOILING POINT AND  $\frac{S}{G}$  SPECIFIC GRAVITY CURVES FOR OIL FROM RUN 21

the composition of the crude turpentine. In these analyses, as in many others, the crude turpentine produced at pressures as high as 70 pounds show a considerably higher value for the specific gravity of the first fraction than do the turpentine produced at lower pressures. This indicates that some substance with low-boiling point and high gravity (above .870 at 15° C.) is produced at the higher pressures; this substance might come from the incipient decomposition of some portion of the resin at the temperature to which it is subjected. The first fractions from the analyses which contained this substance were slightly yellow and had a peculiar odor, different from the rest of the fractions. A treatment with caustic soda reduced the gravity of these fractions but increased the yellow color. It was found, however, that by the treatment of a turpentine like that shown in Figure 2 with caustic soda followed by a distillation it was possible to prepare a refined turpentine which showed no abnormality of the first fraction in color, odor, or gravity. The presence of this substance should not, therefore, introduce any difficulty in the refining process.

Another test for the presence of decomposition products was made on several of the samples produced at different pressures by treating the oil with concentrated hydrochloric acid; a red color produced in this way is supposed to indicate the presence of rosin oil. There was only a very slight coloration of the oils produced at atmospheric pressure, but this coloration increased with the pressure, becoming very marked in the oils produced at 50 pounds and 70 pounds pressure.

#### FRACTIONATION OF THE OIL DURING DISTILLATION

Some very interesting conclusions regarding the details of the manner in which the volatile oil leaves the wood can be obtained by comparing the values of the specific gravity of various portions of the distillate. As was previously stated the specific gravity of the oil was determined from each liter of distillate, or from as many liters as were necessary to furnish the amount of oil required for a determination. Figures 3, 4 and 5 show these values of the specific gravity obtained in Runs 16, 20 and 7, respectively, plotted against the percentages of the total oil obtained.

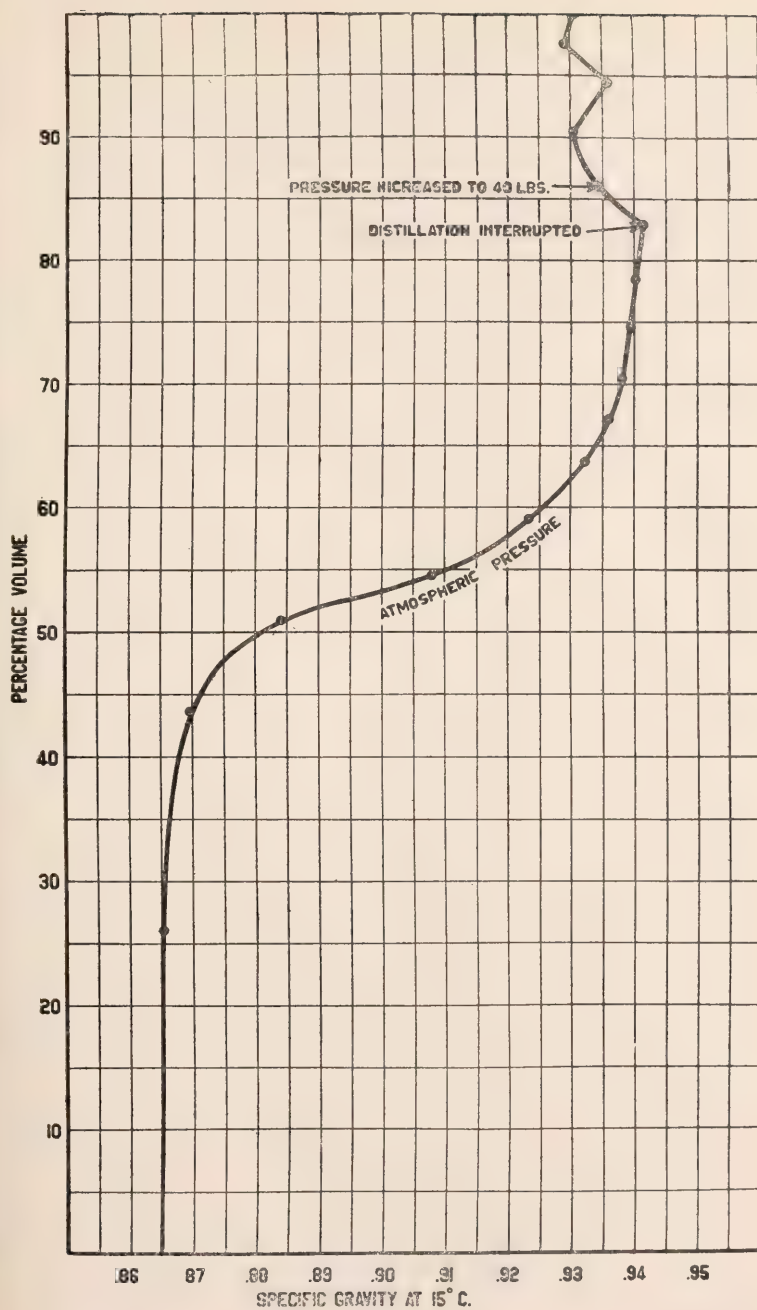


Figure 3. CURVE SHOWING FRACTIONATION OF OIL DURING RUN 16

Figure 3 shows the changes in the specific gravity of the oil obtained during the distillation of a charge of sawdust, first at atmospheric pressure, and then at 40 pounds pressure. The first portions of the oil were nearly pure turpentine, but after about 44 per cent had been distilled the gravity increased rapidly, indicating the presence of pine oil in increasing quantities; when the distillation was from about 67 per cent to 83 per cent completed the oil was nearly pure pine oil. The part of the curve up to 83 per cent resembles very closely the distillation curve which could be obtained from the distillation with steam of a crude turpentine; that is, the presence of the wood seems to have no effect on the manner in which the volatile oils are distilled. A difference is seen, however, in that portion of the curve beyond 83 per cent; after practically all the oil possible had been removed by a continuous distillation at atmospheric pressure, the interruption of the distillation followed by a further distillation under the same pressure produced a small further yield of oil with a lower gravity, and on increasing the steam pressure still more oil was obtained with a still lower gravity. This indicates that both the interruption of the distillation and the increase in steam pressure brought more oil into contact with the steam and that this oil contained some of the low-gravity turpentine material.

A very different behavior is shown in Figure 4, which represents the distillation of chips  $1'' \times \frac{1}{2}'' \times \frac{1}{2}''$  at a pressure of 70 pounds. In distillation under these conditions there was much less tendency for the oil to be separated as it is distilled, the gravity of the very first fraction being higher than that of pure turpentine and the gravity of the later fractions never reaching that of pure oil; that is, the turpentine and pine oil distilled together throughout the run. This indicates that new supplies of volatile oils were brought into contact with the steam more or less continuously throughout the distillation, since otherwise the turpentine would have distilled first and the last fractions would have been nearly pure pine oil.

A still more striking picture of the variation in the gravity of the distillate due to changes in the conditions of distillation is shown in Figure 5; this represents the gravities of different parts of the oil obtained during the distillation of chips  $1'' \times \frac{1}{4}'' \times \frac{1}{8}''$  at



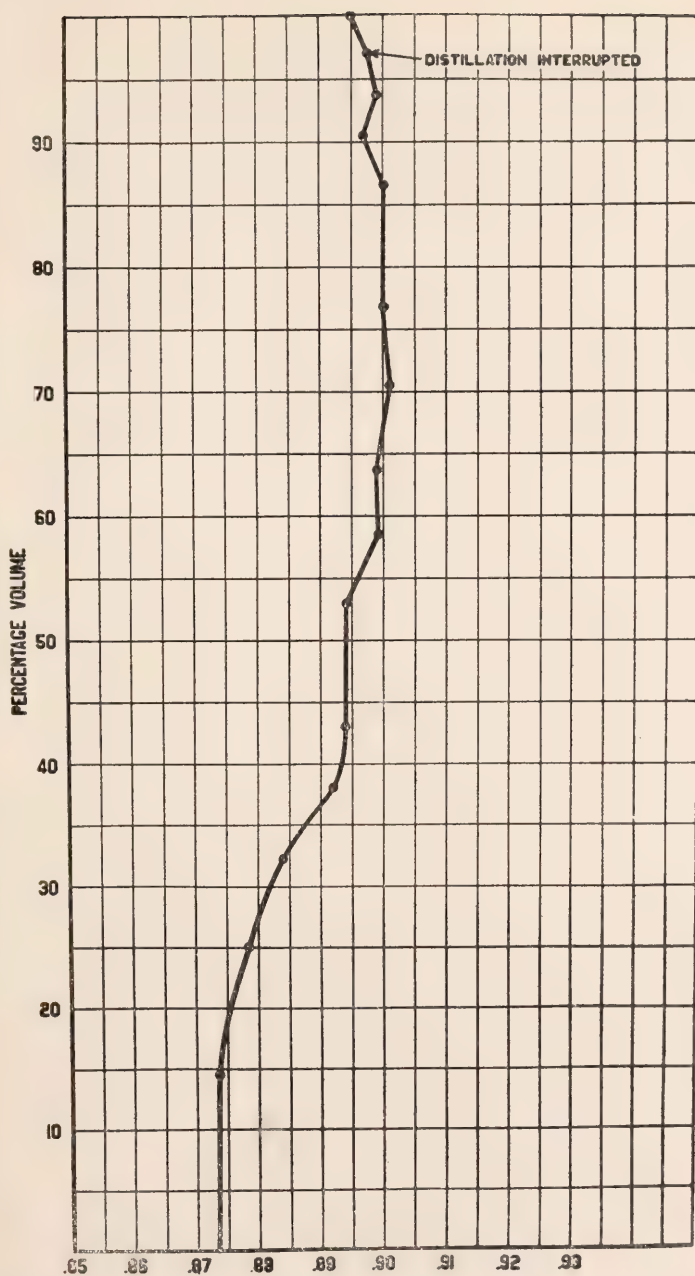


Figure 4. CURVE SHOWING FRACTIONATION OF OIL DURING RUN 20

atmospheric, at 20 pounds, and then at 40 pounds pressure. During the first of the run at atmospheric pressure the gravity gradually increased, but never quite reached that of pure pine oil. By a continuous distillation at atmospheric pressure only about 50.5 per cent of the total oil could be removed, but on interrupting the distillation for about fourteen hours and continuing again at atmospheric pressure 7 per cent more oil was obtained, the gravity of the first part of this 7 per cent being much lower and of the last part only slightly lower than that of the last fraction of the continuous run. On increasing the pressure to 20 pounds, about 16.8 per cent more oil was obtained, the gravity suddenly dropping and then gradually rising during the distillation of this 16.8 per cent. On increasing the pressure to 40 pounds and distilling continuously, a further yield of 19.5 per cent was obtained, the gravity of this 19.5 per cent dropping suddenly at first and then gradually rising. A similar additional yield was obtained by another interruption of the distillation, about 6 per cent more oil being obtained.

Here again the effect of interrupting the distillation and of increasing the pressure are very plainly shown, viz., increased yield of oil with gravity lower than the last fraction obtained before the conditions were changed.

This effect of the increased pressure in increasing the yields is due then to bringing more steam and oil into contact with each other than is possible at lower pressures. This could result either from a penetration of the steam further into the wood at the higher pressures or from a flow of resin toward the surface of the wood due to the decreased viscosity at the higher temperatures. It seems probable that both these have some influence, but the effect of the latter is quite certain, since it was noticeable that in the distillations made at high pressures a considerable amount of rosin would collect in the bottom of the retort or the outside of many of the chips would be coated with thin layers of rosin.

The effect due to the interruption of the distillation and continuing it again under the same conditions can not be explained so readily, but it is probably due to a slow flow of rosin toward the surface or to the diffusion of the volatile oils in the rosin from

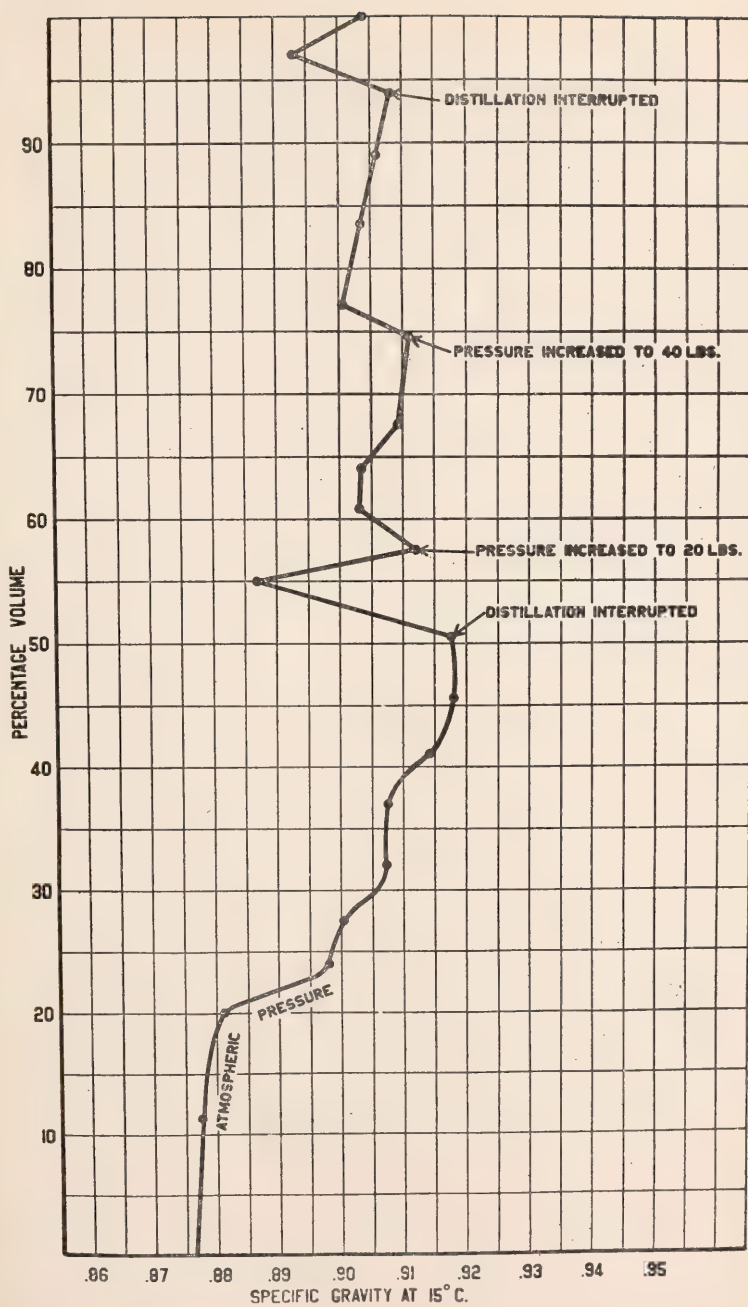


Figure 5. CURVE SHOWING FRACTIONATION OF OIL DURING RUN 7

the interior of the chip to the rosin at the surface from which the oil has been removed.

#### APPLICATION OF RESULTS

The foregoing discussions have considered the effects of the different variables (1) size of chip, (2) pressure of steam, (3) speed of distillation, and (4) end point at which distillation is stopped, on (a) the yield of total oil, (b) the composition of the oil, and (c) the amount of steam required to remove the oil. It can be seen that there should be a certain combination of values for these variables which would give a most economical method of operation for a steam distillation plant; but there are other factors which must be taken into consideration in determining the proper combination of values. For instance, the best size of the chip will not be determined entirely by the effect of size on yield and efficiency, but also by the relative costs of preparing different sized chips and the use to which the chips are to be put after steaming; the best pressure of steam will not be determined entirely by the effect of pressure on yield and efficiency, but also by the relative costs of high and low pressure steam and of apparatus designed for use with different pressures; the best speed for the distillation will not depend entirely upon the effect of speed on the yield of products and on the amount of steam required, but also upon the cost of steam and the overhead charges; the best end point at which to stop the distillation will not depend entirely upon the effect of end point on yield and efficiency, but also upon the cost of the raw material, the value of the products, etc.

Sufficient experimental data have been given, however, so that a knowledge of the various cost factors mentioned above (which would naturally vary a great deal in different plants) would make it possible to decide readily on the most economical methods for operating.

## MODIFIED STARCH

By B. HERSTEIN

*Tariff Board, Washington, D. C.*

The colloidal nature of starch was recognized very early and, like many other colloids, starch is capable of existing in several modified forms. The differences in form here referred to are not those known to be of botanical origin and due to the different plants the starch is derived from. Such differences, although characteristic for each starch, are due only to the size, the number of molecules forming a given granule of starch and their distribution in space. The variations in structure and in optical behavior of starches from different sources are sufficiently explained under some such assumption. Moreover, these variations existing already in a performed condition, are not and cannot be brought about by artificial agencies.

Changes in form on the other hand, spoken of nowadays as colloidal, are of a more far-reaching character; they affect the equilibrium of the aggregation of molecules, and are caused by foreign reagents.

But even with this limitation it is difficult to convey a concrete conception of the term "Modified Starch" as used here, and this is largely due to the peculiar nature of starch as a chemical entity. After a century of intrusive investigation, our knowledge of this most important plant secretion is still very limited indeed in this direction, owing again to the fact that the changes in form which the starch undergoes under the influence of reagents are very gradual, indistinct and almost intangible.

The most specific properties of starch are:

(a) Physical; ability to gelatinize with water or to form viscous solutions therewith, and to show color reactions with iodine.<sup>1</sup>

(b) Chemical; ability to become hydrolyzed with diastase to maltose and with acids to dextrose.

<sup>1</sup>It must not necessarily be a blue color, because there are natural starches, like *panicum miliaceum glutinosum* and *eryzem glutinosum*, which give a red brown color with iodine solutions.



Any product derived from starch showing essentially all or most of these characteristics would come under the heading of "Modified Starch" irrespective of the process used in its preparation, and if this viewpoint is correct the whole group of derivatives, isolated or supposed to have been isolated from starch and constituting gradual disintegration products from starch until the maltose stage is reached, will fall under this classification.

In this sense we would apply the term "Modified Starch" to the "granulose" of mægeli, the "amylose" of Meyer, the "amiduline" of Nasse, the many forms of soluble starch prepared with the aid of either acids or alkalies or of boiling glycerol, the so-called "Thin Boiling" starches, the great number of dextrans including the maltodextrin and amyloextrin, whether they be obtained by torrefaction or by inversion with either acid or an infusion of malt, and, lastly, also the many products isolated under different names by the laborious method of repeated precipitation with alcohol by a host of indefatigable investigators, who tried to shed light on that extremely complex chemical problem comprised within the syllable starch.

There will be little if any objection to this classification as far as the soluble starches are concerned, though some opposition might be expressed with reference to the dextrans. Yet these latter, upon sufficient reflection, will not show more divergence from starch, either qualitatively or quantitatively, than the former. The difference is physical only in either case. While soluble starch differs materially in the fluidity of its aqueous solution from that of starch, the dextrans deviate only in their color reaction with iodine as against that of starch or rather that of standard starch. As shown in preceding foot note, there are starches showing very brown colorations with iodine, or exactly the same as obtained with most of the dextrans. The only other difference between these substances is that the dextrans, as a rule, form apparently perfectly homogenous and transparent solutions with water, while the solutions of soluble and of normal starch are more or less translucent. Chemically, however, they all show the same composition and behavior, especially since it was shown that the dextrans like the rest are hydrolyzed by malt infusions. The principal support, however, for the view expressed by many inves-

tigators and maintained here, namely, that all the products mentioned are but modified forms of starch, *i.e.*, where the original molecule has remained intact, is found in the fact that all the products enumerated show the same rotation of polarized light, equal to that of normal starch. As the degree of disintegration of the starch molecule is, as a rule, in inverse proportion to the rotary power of the products obtained, the substances before mentioned cannot have undergone any considerable breaking up. In view of this, no further justification would seem to be necessary when the term "Modified Starch" is applied here as a generic classification.

In the group of products treated hitherto and comprised within the limits of starch on one side, and maltose on the other, a gradual even if very slow tendency toward degradation and disintegration of the original starch is unmistakable. The processes used in their preparation furthermore make such a disintegration highly probable.

But there exists another group of substances obtained from starch by methods so slow in their effect that any deep going disruption would seem to be precluded. They are substances differing in some physical characteristics from normal starch, though otherwise they are still starch with the same chemical properties, the same optical rotation, where observable, as starch, and showing the same color reaction with iodine as starch. They too are modified starches only. The peculiar feature of these products is their inability to form viscous aqueous solutions or pastes, and in one particular form—to be treated more in detail later—absolute insolubility in either water or alkalies. First to be noted in this group are the products obtained by the action of slightly superheated steam on starch, followed by drying. The starch is in this process rendered almost insoluble in water and is also deprived of the property of forming a paste. Another form of modified starch belonging here and one which might properly be called the anticlimax, to the one preceding, is the product obtained from a fairly thick starch paste when subjected to low temperatures, preferably about 20° C. A spongy mass results, the individual particles of which show distinctly a fibrous structure to such an extent that when it was first observed it was seriously

proposed as a material for paper making, wood pulp being then still unknown. Once fairly dry, no paste can be made of this starch derivative. Within the same category must also be classified the so-called reversion products of starch, the formation of which can be observed in solutions of normal or soluble starch when left standing for some time. The deposits which form cannot be brought in solution again. The starch cellulose isolated by mægeli from starch belongs likewise to this class.

The one particular kind of modified starch belonging to this group to which it is desired to call particular attention is the so-called "non-gelatinizable" starch covered by U. S. Patent No. 982673, issued January 24, 1911. This form of starch perhaps more than any other illustrates the extreme lability of the complex starch grain, because the change in this instance is brought about in a cold and fairly neutral medium, and under conditions which would seem to preclude any far-reaching destructive reaction on the starch molecule itself. This form of starch is easily prepared by bringing starch in contact with a comparatively weak solution (5%—10%) of formaldehyde containing sufficient of an ammonium salt of the heavy acids to form hexamethylen tetramine. The contact should continue for a few hours, the mixture being stirred but not heated. It will be found that, as the time of contact increases, the starch when removed from the mixture and boiled with water becomes less and less gelatinizable and that after the reaction has been completed no trace of gelatinization will be noticeable, but that on the contrary the starch so prepared will—even after prolonged boiling with water—remain absolutely unaffected and sinks to the bottom of the test tube, as any other insoluble powder would. When this point is reached, the starch is separated from the liquid and washed until no reaction is shown in the washing water for either formaldehyde or ammonium salt. As indicated by its name, this peculiar form of starch is characterized by its inability to gelatinize with water on boiling, in fact, if the washing has been complete, a point will be reached when the water having been boiled with the starch will not show any coloration with iodine, although the prepared starch itself, when moistened with iodine solution, will become intensely blue. This form of starch remains unacted upon not only by waters but

relatively strong boiling solutions of caustic alkalies are without effect on it, and it was possible to introduce acetyl and benzol-radicals into the molecule without any outward change in appearance having been noticed. Mineral acids, on the other hand and also some of the stronger organic acids like oxalic, seem to affect this ungelatinizable starch even more nearly than ordinary starch forming dextrose, though the transition through the dextrin form is noticeable and through that of maltose probable.

The mechanism of the formation of this form of starch is interesting. Formaldehyde alone will not accomplish it, still less hexamethylen tetramine. A mixture of formaldehyde and an acid will bring about the desired result to some extent but it must be a strong mineral acid, hydrochloric, sulphuric and nitric acids, in the order given, being available. But with acids alone, a relatively strong solution must be used, while if the corresponding ammonium salt is employed the quantity required is considerably smaller. With a proper mixture of formaldehyde and ammonium salt, it is also possible by the same treatment to render soluble starch, prepared by the Lintner or any other method, entirely insoluble and ungelatinizable, and under certain conditions even the dextrins will show the same result.

There is much reason for the statement and little to the contrary that the reaction described above does not affect in the least the chemical composition of the starch, but merely extends to the surface of the starch granule, hardening it and making it insoluble in the same way as the formaldehyde reacts upon gelatin and other nitrogenous organic colloids, although in this instance the necessary presence of an acid or still better of an ammonium salt as a contact substance, or catalyzer, is interesting. The colloidal character of the reaction is undeniable. This non-gelatinizable starch retains traces of formaldehyde very tenaciously even after prolonged washing as distillation with acids show.





# RESOURCES AND CONDITIONS IN THE STATE OF WASHINGTON FOR PAPER MAKING

BY GUY C. HOWARD  
*Everett, Washington*

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## INTRODUCTION

The scope of this paper is to present some general information regarding the resources and conditions which exist in the State of Washington affecting the question of the development of paper-making and allied industries. Features of the situation will be taken up which would naturally be of interest to parties anticipating the investment of capital in the development of these industries, but details regarding the technology and commercial phases of any particular line of paper making will not be gone into, as these are from necessity a matter of detailed investigation preliminary to actual investment. The resources of the State are such as to invite development, and paper making will be one of the leading industries of the future, but to insure this development taking place so as to result in the most permanent and lasting benefits it must be carried on along natural and reasonable lines and with a full knowledge of conditions as they exist. It is to be desired that this paper may be the means of bringing the resources of the State to the favorable attention of those interested in the paper industry and at the same time give some idea of the situation as regards markets, manufacturing costs and investment required.

## RAW MATERIALS

Woods of various kinds exist throughout the State in abundance. Spruce, hemlock, fir and cottonwood are principally confined to western Washington, while pine predominates in the eastern part of the State. All of these species are being used at present to make paper of various grades. The slabs, edgings and sawdust from the extensive lumber industries of the State furnish an enormous quantity of material of prospective value,

and particularly for special grades not now being made. The grain regions of the central and eastern portion of the state provide a very large tonnage of straws.

These raw materials exist in ample quantity to support an extensive development of the industry. In general they are easily accessible to transportation and power, but this is not true in the case of cottonwood, which is of particular value in book and magazine papers. The manufacturers in this line are already confronted with the necessity for reforestation to assure a future supply of this species.

#### POWER RESOURCES

The water power development in the State is only in its infancy. Many power sites exist of which some have already been developed on an extensive scale. The State as a whole, and particularly the region west of the Cascade Mountains — known locally as western Washington — is destined without question to be a region of cheap and abundant power. Ample evidence of this fact is apparent on every hand. Conditions are such, however, as to lead to the development of this power in large projects for the commercial sale of power rather than in the line of small individual power sites.

Fuels for steam power are available in abundance and in several forms. The extensive oil fields of California and the easy means of transportation by tank steamer make oil a cheap and reliable fuel supply. Enormous quantities are consumed at present for power plant and locomotive use. The coals mined in the state are available to a limited extent for power purposes and can be gotten in grades from a good bituminous down to a lignite. The Alaska coal fields when opened up and developed, will be easily accessible to the state and assure a permanent and cheap fuel supply. The wood refuse from the saw mill industry, under favorable conditions of equipment to handle, provides a very cheap fuel for certain locations.

#### MARKET CONDITIONS

The question of a market for a manufactured product as paper is one easily overlooked, and especially so in developing an industry remote from congested population. It is of course a matter

of the most vital importance. With the present freight rates the market accessible to paper made in Washington, in equal competition with Eastern mills, comprises the States of Washington, Oregon, California, Idaho, Utah and Nevada. The last census report gave Washington a population of a little over one million people, and showed the combined population of the above named states to be approximately five million people. This amounts to but about five per cent of the total population of the United States. This population is increasing rapidly and undoubtedly will continue to do so, still as compared with conditions in the Atlantic Coast States, the home market for an industry in this region has distinct limitations. Furthermore, in most grades of paper made in this section the disposition of the manufacturer is to keep pace with the increase in home consumption by an increase in his capacity, which is a natural thing to do, as in general the plants are small. A home market that will absorb at least 65% of a paper plant capacity is essential to success in this region as in most others, and the more nearly the full capacity output can be marketed in home territory the better the position of the manufacturer.

As regards export trade, the experience of the manufacturers here has been that they cannot at present compete on price in the world markets. This is a condition which will improve as time goes on, but at present the state is a region of cheap raw materials and cheap power, but one of high cost for labor, supplies and equipment, and consequently high investment per ton of production. In competition with the world in export trade the disadvantages of the latter items more than offsets the advantages of the former, so the cost of production is distinctly higher in the West than in Eastern and European mills.

The opening of the Panama Canal will be a factor destined ultimately to favor the paper industries of Washington, but the immediate effect will be to the advantage of Eastern mills. The present selling price of paper on the Pacific Coast is based on the selling price in the Eastern market plus the freight to Pacific Coast points. The freight differential now amounts to \$15.00 per ton, but with the opening of the canal this will be reduced to \$9.00 per ton or less, so the Washington manufacturer

will be confronted with an immediate reduction of at least \$6.00 per ton in the selling price of his product. This reduction must be offset by a reduction in his manufacturing costs, and while the reduced freight from eastern points will lower somewhat the cost of his chemicals, supplies and repair equipment, still it will not make him any nearer the base of supplies in these items, nor reduce the necessity of his carrying large stocks to prevent loss through shut down. The opening of the canal will of course afford a cheap and direct transportation to Atlantic Coast points, but this will only be of advantage to the Washington manufacturer when an increase in cost of raw materials or labor costs in the East establishes a balance so the advantage of cheap raw material and power in Washington more than offsets cheaper cost of labor, supplies and equipment in the East. This will come ultimately but the Washington paper manufacturer can hardly expect to compete on Atlantic Coast points for some years to come. The increase in the population of Washington due to direct European immigration will be a distinct factor in the growth of the western home market.

#### LABOR

The cost of all kinds of labor in Washington is 33% or more higher than in the East and the direct bearing of this is an increase in manufacturing cost of production. Any change in this labor situation will be gradual at best and only on certain classes of unskilled labor affected by direct immigration from Europe through the Panama Canal can any reduction on the present scale be looked for. A reduction in the difference between labor cost in the Eastern and the Western mill is more likely to come from an increase in cost of skilled labor in the East rather than a lowering of present wages in the West on this class of labor.

#### EQUIPMENT AND SUPPLIES

Most of the equipment and supplies used in the paper industry come from the East or Europe, which means a materially higher cost to the Washington manufacturer on chemicals, wires, stones, fillers, repair parts, and initial equipment. This location of a plant two or three thousand miles from a base of supply ne-



cessitates keeping a much larger stock of supplies and repair parts on hand at all times to safeguard against shut down. Both the above items are factors in the cost of production and must be taken account of by the Washington manufacturer.

#### PRESENT INDUSTRIES

The following named plants are already operating in the region that would be a "home" market for a Washington manufacturer, and give some idea of the situation as regards competition in the various kinds of products:

Everett Pulp & Paper Co., Everett, Washington. Book, magazine and chemical writing.

Willamette Pulp & Paper Co., Oregon City, Oregon. News.

Crown Columbia Pulp & Paper Co., mills at Camas, Wash., Oregon City, Oregon. News, wrapper, fruit tissue.

Hawley Pulp & Paper Co., Oregon City, Oregon. News and fruit tissue.

Lebanon Paper Co., Lebanon, Ore. News and wrapper.

Inland Empire Paper Co., Spokane, Wash. News and fruit tissue.

Floriston Pulp & Paper Co., Floriston, California. News and fruit tissue.

Pacific Paper & Boxboard Co., Seattle, Wash. Boxboards.

California Paper & Board Mills, Antioch, California. Boxboards and sheathing paper.

#### LINES FOR DEVELOPMENT

On the grades of paper already manufactured here further development should be a result of careful investigation, in view principally of the present limitations of the home market. In some lines the field will be found amply covered, in others opportunity may exist for new plants. On lines not already manufactured here the field is a promising one.

The particular resource that invites development and use is the waste from the lumber industry in the form of sawdust, slabs and edgings. With the present cost of cord wood for pulp it is not economical to use sawmill slabs to make into white stocks owing to the high cost of perfectly cleaning and freeing from bark.



Neither is the wood resinous enough to work for turpentine by the steam process as practised in the long leaf pine region of the South. There is, however, a large amount of this waste that can be easily segregated to give a raw material sufficiently clean and of good fibre length for many purposes.

#### CONCLUSION

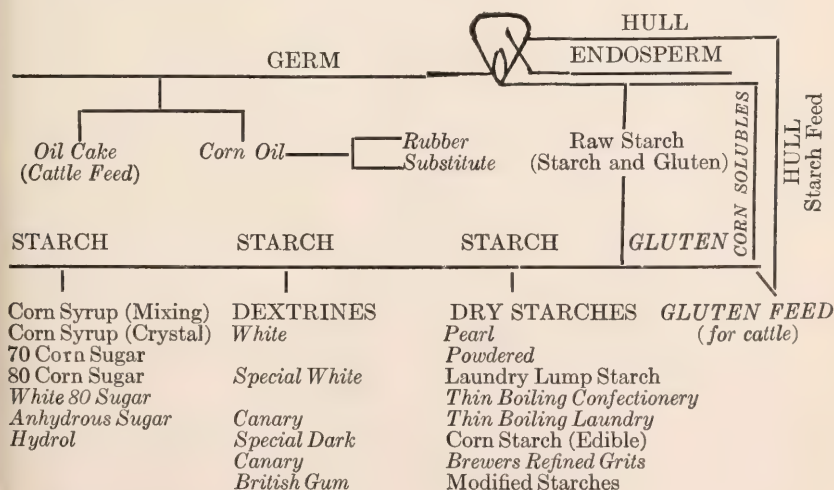
In conclusion it may be justly said that the State of Washington has abundant raw materials and ample cheap power, both steam and water, to maintain an extensive development of the paper industries. The determining factors in the success of plants making any grade of products is the present limitations of the home market and the higher manufacturing cost per ton of output than in Eastern mills, both of which items are becoming more favorable from year to year. In several grades of products not being manufactured at present, an attractive opportunity exists for immediate investment and the whole field warrants investigation, as the State is destined to be known as one of extensive paper industries.

# THE INFLUENCE OF BY-PRODUCTS UPON THE DEVELOPMENT OF THE INDUSTRY OF CORN PRODUCTS

BY H. C. HUMPHREY  
*Hackensack, N. J.*

The manufacture from the kernel of corn (*Zea Mays*) of the various products which are now exploited has been of slow growth. The first attempt to produce starch from corn was made by Thomas Kingsford, who after several years' discouraging experiments, succeeded in making corn starch of excellent quality, both for edible and laundry purposes, and established in 1848 the first corn starch works at Oswego, N. Y.

In order to clearly understand the problems which have had to be solved in the manufacture of corn products, and to follow historically the steps which have been taken in the utilization of every portion of the kernel, the following diagram has been prepared, which shows the constitution of the corn kernel and the comparative development.



Roman — Products made before 1881.

Italics — Products made after 1881.

It is not the object of the present paper to enter into the details of manufacture, but simply to point out the influence of the utilization of by-products on the development of this important American industry, I will briefly describe the process so that the matter may be clearly understood.

As the aim of the early manufacturer was to produce starch alone, it was only necessary to soften the grain by steeping in warm water or water to which a small amount of alkali was added, whereby an incipient putrefaction of the germ and nitrogenous substance was engendered, and then by grinding and sieving to separate the hull and part of the germ from the endosperm. The ground germ and hull was found to be excellent cattle feed, and until 1881 sold in a wet state under the name of "starch feed." The endosperm, which contains the starch and gluten, was then, by a process of washing, in which alkali and water were employed, and of settling and decantation, or by running over the so-called tables, separated into starch and gluten. The gluten was for the most part wasted. The starch was then either dried and made into laundry and edible products, or transformed into corn syrup (glucose) or corn sugar (grape sugar).

The modern process of corn starch manufacture was developed, through the labors of Dr. Arno Behr, and the author working partially along lines, first suggested by Chiozza, in which sulphur dioxide was employed in the steeping of the grain. Through the efforts of Messrs. F. O. and E. A. Matthiessen, this process was first established in 1881 at the Chicago Sugar Refining Company.

By this process the corn is softened in warm water to which a trace of sulphur dioxide is added. The sulphur dioxide not only prevents during the steeping the decomposition of the germ and gluten, but partially dissolves the intercellular tissues, thus rendering the component parts more easily separated by the subsequent operation. The softened corn to which water has been added is crushed in a mill, so constructed that little injury is caused to the elastic germ. The mass is then run into long tanks provided with appropriate conveyors and skimming apparatus, filled with starch liquor of about 8° Baume. The germs, containing a large amount of oil float to the top and are run over sieves. The hulls being heavier, sink to the bottom and are carried over sieves. The germs and hulls are thus respectively separated from the starch

liquor, made up of crushed endosperm (gluten and starch). This latter is now separated as in the older method, by running over the tables.

In 1881, the gluten, which was formerly run to waste, except occasionally, when it was carried off by the farmers in barrels and fed to the stock, was for the first time recovered in a dry form by a method consisting of filter pressing, drying and grinding. A few years after the hulls, which had been sold in the wet form, were incorporated with the gluten, dried and ground, thus constituting gluten feed.

In 1893-1894, the corn solubles, contained in the water in which the corn had been steeped, were first concentrated and mixed with the gluten feed. At this time only about one-half of the solubles of the corn were recovered, the portion remaining in the steeped corn after the removal of the steep water being lost by washing in the subsequent processes. In 1908, there was introduced a continuous diffusion system, whereby the corn solubles were concentrated in the steeping, and as a result an additional amount of dry corn solubles was saved.

A stage in the development of this industry has now been reached where practically all of the original raw material is recovered; any future advance must be, therefore, in modifying the products or extracting from them materials which are better fitted for some special use in the arts, and, therefore, commercially of greater value. A new modified form of starch, as described in U. S. Patent No. 855,599, is an apt illustration of work that is being done along these lines. However, corn solubles appear to present the most promising field in this respect. They are now incorporated with the gluten feed. In order to afford an insight into the possible uses for which this material is fitted, the following average analysis of corn solubles on a dry basis is here given:

|   |        |
|---|--------|
| N x 6.25                                      | 40.00% |
| Reducing Sugar, as Glucose                    | 25.00% |
| Phosphoric Acid ( $P_2O_5$ ) Organic (Phytin) | 4.80%  |
| Phosphoric Acid ( $P_2O_5$ ) Inorganic        | 2.50%  |
| Sulphuric Acid ( $SO_3$ ) Combined            | 1.66%  |
| Hydrochloric Acid (HCL) Combined              | .54%   |
| Calcium Oxide (CaO)                           | 1.00%  |
| Magnesium Oxide (MgO)                         | 2.71%  |

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|   |                                 |
|---|---------------------------------|
| Potassium Oxide ( $K_2O$ )              | 5.76%                           |
| Sodium Oxide ( $Na_2O$ )                | 1.12%                           |
| Acidity (Phenolphthalein as Indicator)  | 181. CCSN/L<br>NaOH to 100 gms. |
| Alkalinity (Methyl Orange as Indicator) | 55 CCSN/L<br>HCL to 100 gms.    |

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The 40% of nitrogenous material calculated as protein is in the form of amino and other compounds, resulting from the cleavage of the protein during the process. These non-protein bodies, according to the latest nutrition investigations, are of much greater value than was formerly supposed, being now shown to be equal to protein in "maintenance," although not in "production."

The organic phosphorous compounds have not as yet been closely studied, but are doubtless similar to the phytin of other grains.

The following possible commercial uses for these corn solubles have been suggested: As a fertilizer, the contents of 7.65  $NH_3$  6.8%,  $P_2O_{10}$  and  $K_2O$  gives it a fertilizing value of a little less than is now obtained for it in its present form as a cattle feed.

As a yeast food, preliminary experiments have already been made, which seem to show that it is of substantial value to the fermentation industries. It may also find use in the manufacture of compressed yeast.

As a food, corn solubles mixed with corn syrup may be made into a refreshing beverage. The amino compounds, as well as the possible therapeutic value of the organic compound, may add to its nutrition value.

Appetizing soups have been prepared. These resemble the vegetable extracts which are now being made from yeast and various vegetables and grains, and are found on the market alone or or mixed with beef extracts.

These are some of the possible uses which in the future may be found for this by-product, and as there are about 100,000,000 pounds of dry corn solubles produced yearly, the importance of this subject is evident.

Previous to 1881, the products obtained were starch and starch feed, and it is safe to say that their total yield from corn (dry basis)



was not more than 70 to 75%. The large amount of valuable material thus wasted, which consisted of gluten and corn soluble, and a part of the germ, being in its nature highly nitrogenous, was very putrescible, and grossly polluted the streams into which it flowed, and gave rise to complaints and many law-suits. The plants were necessarily built of moderate size and mostly in small towns, therefore it was impossible to reap the economical advantages possessed by the centrally located factories of today.

Formerly the price of corn was so low that it was possible to obtain satisfactory returns on the investment even when 25% to 30% of the raw material was wasted. Of late years conditions have greatly changed. Corn has advanced in price and doubtless will continue to do so. It is estimated that of the annual corn crop of about 3,000,000,000 bushels, 85% to 90% are fed on the farm, being transformed into cattle, hogs, poultry, milk, butter and eggs, and as these latter provisions are yearly increasing in price, there seems a strong probability that in the future the farmer will sell less and that there will be a gradual increase in the value of the marketed corn.

On the other hand, the price obtained for the products, starch, corn syrup, corn sugar, is to a certain extent limited by the price of their natural competitors, which are starch and glucose from the potato, sago cassave and other starch producing plants, and sugar, syrup and molasses from the cane and beet.

In order to conduct the business on a profitable basis it is necessary to conduct it on a very large scale. For instance, a factory recently erected has a daily capacity of 45,000 bushels of corn, therefore the location must be where there is a central grain market of sufficient size to furnish daily such an amount of raw material. Again it must be located where the lowest freight rates can be had, where the shipping facilities are the most favorable and labor the cheapest. Besides these advantages of location, the process must be conducted and controlled by the most modern mechanical and chemical methods. Yet with all this care and vigilance, the corn starch industry could not exist today were it not that the by-products had been utilized to the fullest extent, for the present cost of corn is nearly as great as the price obtainable from the recovered starch and starch feed, had no other by-products been saved.



COMMERCIAL CELLULOSE CHEMISTRY,  
PARTICULARLY RELATING TO CELLULOSE ACETATE

BY HARRY S. MORK

*Boston, Mass.*

Although the title of this paper is exceedingly comprehensive, it should be explained as a preliminary that, while it is intended to cover in a general way some of the points and problems embraced by the broad subject, it is the intention chiefly to cover more in detail that special corner of cellulose chemistry which has received much attention during the past decade, but which has been especially the subject of highly active industrial research during the past five years, both in America and Europe; in other words, the cellulose esters of organic acids, particularly cellulose acetate.

The literature on cellulose and its chemistry is far from being voluminous, although it has had two distinct contributions in the past two or three years in Worden's "Nitrocellulose Industry" and Schwalbe's "Die Chemie der Cellulose." Why there has not been more intimate study of the subject with more recorded data is not difficult to answer. Primarily, notwithstanding that cellulose, as the chief component of cotton, or flax, or hemp, or wood, and in fact all forms of plant life, is scattered over the face of the earth in the greatest profusion and abundance and is of the most fundamental importance to the well-being of human life, the study of its composition and reactions is really a small and highly specialized branch of the great science of chemistry. This is no reason for neglect, if the study of cellulose has indeed really been neglected, but if we stop to think of the reactive inertness of cellulose, of the great complexity of aggregates of this type, and of our deficiency of knowledge of the fundamental laws governing the behavior of such complexes, and when in addition in this particular case we also consider that the synthesis of cellulose offers no inducements to the pure chemist, it is not to be wondered at that more effort has not been concentrated on

the study of the ultimate composition of cellulose, or of its exact structure. As might be expected, there has been much conjecture, much theorizing and in consequence much controversy over what the probable structural formula of cellulose might be, but the opinion is here voiced without hesitation, although others may perhaps have previously expressed it, that the available data at present is all too insufficient to justify even a serious assumption of the probable chemical structural make-up of cellulose.

Now cellulose is a material of the first order for technical application, and while it is impossible to say to what degree the deficiency of composition data has retarded its industrial developments, it is nevertheless true that nearly every known chemical reaction in which cellulose participates has been practically utilized with much profit and benefit to the community. Realization of this fact has at last come to chemists, and the technical cellulose field is now being explored with really remarkable endeavor.

Several known facts of first importance should be borne in mind and they are here referred to because they are pertinent to cellulose chemistry in its broad aspect, and because they have particular bearing on the proper understanding of the physical and chemical properties of the cellulose esters. These facts are: first, that cellulose is a molecular aggregate of high complexity, and in consequence can pass through various reactions with the possibility of producing an indefinite number of products of like empirical composition, but varying in the degree of aggregation and, therefore, in physical properties; second, that cellulose as such is not soluble in neutral solvents, and either acids or alkalies, so far as we now know, must be present in the different reactions in which cellulose participates; third, that all cellulose reactions seem to require, or are accompanied by, either hydration or hydrolysis, prior to, during or subsequent to, the general reaction.

To the first of these facts, complexity of the cellulose molecule, can be attributed the now firmly established precedent, that a very long period of experimental development must be expected to ensue between the discovery of a new cellulose reaction and the time when it shall be sufficiently perfected to be considered a positively demonstrated practical application, pro-

vided of course that the reaction is of that class which permits of such development and application.

Through just such a trying period has passed the nitration of the cellulose, and the formation of viscose, or cellulose xanthogenate. From a like period the acetylation of cellulose has not yet wholly emerged, but now, forty-three years after Schutzenberger recorded his experiment of producing cellulose acetate by heating cotton cellulose with acetic anhydride in a sealed tube, and nearly twenty years after Cross and Bevan utilized the more reactive recovered cellulose from their viscose process as the cellulose base for acetylating, now indeed has the perfected present-day cellulose acetate become a controllable industrial material with not only its limitations but its great possibilities well recognized.

As has been stated, that cellulose could be acetylated has been known for nearly fifty years, but the real father of the modern cellulose acetate industry is A. P. N. Franchimont, who found, and publicly disclosed in various scientific journals about thirty years ago and later, that cellulose could be acetylated by acetic anhydride with great facility provided a small amount of sulphuric acid was added to the reaction mixture, and who, moreover, showed that the quantity of sulphuric acid and the conditions of the reaction influenced the physical properties of the cellulose acetate produced.

Nowadays all cellulose acetate is made by this general method of adding an assisting or condensing agent to the reaction mixture consisting of cellulose, or modified cellulose, and acetic anhydride, and the different patented processes vary either in the form of cellulose used, the nature and quantity of the condensing agent, the general reaction conditions of time and temperature and the method of recovery of the acetylated cellulose. With the exception of the Cross and Bevan acetylation method of acting on recovered cellulose from viscose by means of acetyl chloride and an inorganic acetate, essentially all the contributions to the patent literature on cellulose acetate covering the manufacture of this product have been issued subsequent to 1899, and they all follow the general basic method of Franchimont, and must therefore be interpreted as being valid within the limi-



tations of the conditions specified, but provided of course that these conditions are true in fact, and not previously anticipated.

When cellulose is acetylated, using of necessity acetic anhydride and diluting if necessary with acetic acid, the cellulose acetate passes into solution as fast as formed and is recovered from the solution in a powdery, granular or horny mass by precipitation with water or some other non-solvent of the ester such as a hydrocarbon or carbon tetrachloride.

Prior to about seven years ago the granular, amorphous form of cellulose acetate was the only variety known, but about 1905 it was learned that the acetylation could be conducted in a bath in which the ester was insoluble, and the product so produced retained the general physical form of the initial cellulosic material, so that if cotton yarn is used, the end product is cellulose acetate yarn.

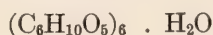
A process of this character has positive inventive features which are obvious and which do not pertain to any of the other processes, such as producing acetylated celluloses of fibrous or other specific forms, and the ease of solubility, but it has also other advantages which are not obvious. Among these are ease of control, with the possibility of standardization of products, practically theoretical yield, and the ability to retain the molecular aggregation of the cellulose to a far higher degree than seems to be possible by any of the solution processes. This last is of fundamental importance because the degree of aggregation primarily determines the strength of the commercial products which can be made from the cellulose acetate.

On this account, if for no other, it is believed that the cellulose acetate of the future will all be made by the fibrous method. Fortunately a relative measure of the aggregation is to be had in the viscosity of solutions of cellulose acetate in a standardized solvent.

Cellulose compounds in general show so many solubility-peculiarities and possible property-variations that it is not to be expected that the acetylation of cellulose is by any means a simpler procedure than nitration for instance. Speaking particularly of the fibrous acetylation of cellulose, it requires careful adjustment of the proportions of reagents, of the time and tem-

perature conditions and of the character of the original cotton to be acetylated in order to secure the maximum control of product which the process affords.

Referring entirely now to the process of preparing fibrous cellulose acetate in a high degree of aggregation, — in the first place the cotton cellulose to be acetylated must be carefully prepared and not structurally weakened by the cleansing or bleaching process. This high grade cellulose is then subjected to a preliminary treatment with acetic acid, water and a condensing agent, as for example sulphuric acid, under particular conditions whereby, as far as we now know, the cellulose is hydrolized so that one molecule of water is added for every thirty-six atoms of carbon, or for every six groups of the formula representing the empirical composition of cellulose as follows:



This initial hydrolysis seems to be essential for a controllable acetylation, and the conditions of the hydrolysis are vitally important. After the preliminary treatment, the excess of reagents is removed mechanically and the acetylation proper takes place in a bath consisting of acetic anhydride and a restraining agent, usually benzol, but the bath otherwise modified in a way which technical experience has demonstrated as being advantageous for producing the best quality of cellulose acetate. The temperature is carefully controlled throughout the acetylation, and all the other conditions are adjusted from start to finish, so that the end product shall be cellulose triacetate of desired solubility and viscosity. Compared with most chemical reactions, the process is a slow one, for it is rarely complete inside of eight hours, but best results are not usually obtained by an acetylation which takes much less than eighteen hours. The reaction proceeds so slowly that at any time during its course a small sample can be removed and tested to see if it meets specification. When the acetylation is complete, the mixture of acetic acid and benzol is drained from the cellulose acetate, which is thoroughly washed free from acid and dried and the acetic acid and benzol can be separately recovered by distillation or otherwise and utilized again. During acetylation, the fibre bulks up greatly, which is

to be expected when it is realized that the original cotton increases approximately 75 per cent in weight in its conversion into cellulose triacetate. Theoretically, 100 parts of dry cellulose should yield 178 parts of cellulose triacetate, and in a properly conducted fibrous acetylation practically this yield is regularly obtained. It used to be considered at one time that ordinary acetylated cellulose was tetracetate of cellulose, but now it is generally conceded that the maximum degree of acetylation obtainable corresponds to cellulose triacetate. The mistake has been in part due to saponification methods. By boiling with half-normal alcoholic potash solution, saponification values are frequently obtained which correspond fairly closely with calculated figures for cellulose tetracetate, due undoubtedly to further decomposition of the cellulose by the alkali. With half-normal alcoholic potash diluted with an equal volume of water, true values are obtained after one to two hours boiling. This seems to be a rapid and accurate method.

A point is here recorded as being of interest in the pure study of cellulose chemistry. It does not seem possible to acetylate cellulose directly by acetic anhydride alone without a condensing agent, except at very high temperature, and then there is some question whether at these temperatures the cellulose is not subjected to partial decomposition whereby the reaction is enabled to take place. This occasions some doubt as to whether there are in normal cellulose any free hydroxyl groups, which uncertainty is by no means clarified by the observation that cellulose recovered from cellulose triacetate by saponification does not seem to be any more easily acetylated by acetic anhydride alone than is the original cellulose.

As nearly all the practical applications of cellulose acetate require it to be either gelatinized or dissolved, the solvents of cellulose triacetate are a matter of primary consideration. These solvents are not generally the same as those of cellulose nitrate and there are relatively few in common. In the main, the chief solvents of cellulose acetate are of two classes, — chlorine compounds and phenols. There are a number of other solvents outside these classes along which is acetone. The question of acetone solubility will be taken up now because it introduces another

peculiarity of cellulose acetate. If the acetylation is brought about by a relatively small percentage of condensing agent, as for example sulphuric acid, the cellulose acetate produced thereby will be only slightly, if at all, soluble in acetone; if the percentage of sulphuric acid is increased, the solubility in acetone is increased. Better yet, if after the cellulose acetate has been formed it is digested for some time with aqueous solutions of mineral acids of moderate strength, it will become entirely soluble in acetone. Because, after acetylation, the cellulose acetate is always immersed in water to free it from the acids used, the above described after-treatment always takes place in the practical manufacture of cellulose acetate, and because it takes place more rapidly when the aqueous acid is stronger, accounts in a great degree for the fact that cellulose acetates prepared with a larger percentage of condensing acid show greater acetone solubility than those prepared with only a relatively small amount. The change to acetone solubility has been inferred to be occasioned by hydration or hydrolysis of the ester, but no concrete data has as yet been advanced to verify this inference. This is true, however, that the acetone soluble cellulose acetate shows a wider range of solubility in other solvents than does the kind not soluble in acetone.

Returning now to the two general solvent classes previously mentioned; of the chlorine compounds, chloroform and tetrachlorethane or acetylene tetrachloride are the most important, the latter being a much more powerful solvent than chloroform. Methylene chloride, ethylene chloride, epichlorhydrine, dichlorhydrine, methyl chloracetate, ethylenechlorhydrine, acetochlorhydrine, ethyleneacetochlorhydrine, dichlorethylene, trichlorethylene are some of the other chlorine solvents of varying degrees of solvent power, some of them only solvents of the acetone soluble acetate and some only exercising solvent power in the presence of limited quantities of methyl and ethyl alcohols. Neither methyl nor ethyl alcohol is, strictly speaking, a solvent of cellulose acetate, but these alcohols added to most of the chlorine solvents increase marvelously the solvent power of the solvents, creating in some of them general solubility where otherwise it is limited to certain kind of cellulose acetate, and causing in the case of others marked decreases in the viscosity of the



solutions, with the possibility of producing flowable solutions of high concentrations. The viscosity reductions are, however, not so great with ethyl alcohol as with methyl alcohol.

Phenol, or carbolic acid, is perhaps the most powerful of all the solvents of cellulose acetate, but other phenols like cresol, thymol, guaiacol, carvacrol, benzyl phenol, amyl phenol, and resorcin are also excellent solvents. One measure of the solvent power of a phenol is the degree to which a given cellulose acetate solution in it can be diluted with benzol without causing permanent coagulation. Most peculiarly, ethyl or methyl alcohol cannot be added to phenol solutions of cellulose acetate to anywhere near the extent that benzol or its lower homologues can be added.

Of some of the other fairly strong solvents mention might perhaps be made of formic acid, acetic acid, pyridine, aniline, methyl formate, methyl lactate and methyl and ethyl acetoacetate. There are also perhaps a few solvents of very limited solvent power like diacetone alcohol and methyl and ethyl acetates. Amyl acetate and ether alcohol mixtures, ordinary solvents of cellulose nitrate, are not solvents of cellulose acetate.

It is not the intention of this paper to discuss at any great length the commercial applications of cellulose acetate, and yet perhaps a few words on this branch of the subject may be of interest at this time. Cellulose acetate is essentially adaptable for the manufacture of all the products for which cellulose nitrate can be used, except of course explosives, and because the acetate is so slowly combustible it has even a much larger field of usefulness. Many of these uses are now in the course of technical development, coincident with which is a gradual lessening of the cost of production.

It will not be very long before the highly inflammable and hazardous celluloid moving picture film will be entirely replaced by the safe cellulose acetate film. A step has been made already in this substitution, and were it not perhaps for unpreparedness and monopolistic suppression, the substitution would be complete by now.

As an effective insulation of very fine wire, cellulose acetate has been technically applied for over ten years, having certain mechanical advantages possessed besides only by cellulose nitrate,



but having the additional virtue of far greater stability and permanence at much higher temperatures. For the manufacture of waterproof artificial silk and imitation bristles, cellulose acetate is unique. The nitrate is not at all suitable for these purposes because of its hazardous inflammability in the necessarily fine state of division of the material in these applications, and if the inflammability is removed by denitration all the waterproof properties are also lost. For the manufacture of ready mixed bronze and gold paints, a cellulose acetate solution in acetone is peculiarly suitable, while cellulose nitrate solutions are not, particularly because the latter corrodes bronze powder, while the former does not. Again, for waterproofing aeroplane cloths and imparting rigidity, cellulose acetate is well adapted, while the nitrate is too hazardous to use. It is expected that ultimately cellulose acetate will substitute effectively for many of the present applications of celluloid, but it is not intended by any means to convey the impression that celluloid will ever be completely eliminated, for it certainly has many uses for which cellulose acetate cannot be adapted, just as there are many more applications than have been mentioned in which cellulose acetate products will have a distinct field of their own.



THE OCCURRENCE OF PENTOSANS AND HYDRO-  
LYZED PENTOSANS IN CORN (MAIZE)  
AND CORN PRODUCTS

BY CHRISTIAN E. G. PORST  
*Coytesville, N. J.*

The chemical laboratories in the factories which manufacture corn products control the daily work by a number of tests—starch, protein, fat, etc.—in intermediate as well as in finished products, but hitherto little or no attention has been paid to the pentosans.

It is the purpose of this paper to trace the pentosans from the corn kernel through the various products of disintegration down to the finished products, to see to what extent they are present.

Therefore I will have to outline the process of disintegration but shall do that as briefly as possible and refer readers who want further information to a more thorough description of the American industry of corn products which has been given by T. B. Wagner in the *Journal of the Society of Chemical Industry*, Vol. XXVIII, 1909, No. 7.

I have used in my work Counciler, Tollens and Krüger's phloroglucin method for the determination of total pentosans, Votocek, Tollens and Ellet's alcohol extraction for the determination of the methyl pentosans. Results are given according to the tables calculated by Tollens, Kröber and, Ellet and for, the sake of uniformity and comparison, all results are given as pentosans and methyl pentosans figured on dry basis.

The method requires that the phloroglucin added for precipitation shall be twice the amount of furfural expected; therefore I have made preliminary tests for each individual group of material, using an excess of phloroglucin, but otherwise the results were not considered. Where determinations were made in products with excessive moisture, the first portion of hydrochloric acid added was stronger than the 1.06 sp. gravity prescribed in the method and then of such calculated strength that the right gravity was obtained.

To avoid any oxidation of the phloroglucid, large glass-stoppered weighing bottles were used to place the Gooch crucibles in while cooling in desiccator and weighing.

A number of determinations were made, but, the corn excepted, only the average results are given here. As it is interesting to see in what proportion to each other pentosans and methyl pentosans are present, this relation has been figured out as parts in 100 parts total pentosans for each of the various products.

| 1. Corn. |                    |          | Dry Basis |                    |       |
|----------|--------------------|----------|-----------|--------------------|-------|
| Pentosan | Methyl<br>Pentosan | Moisture | Pentosan  | Methyl<br>Pentosan | Total |
| 4.38     | .536               | 19.50    | 5.44      | .666               | 6.106 |
| 4.69     | .780               | 18.50    | 5.75      | .957               | 6.707 |
| 4.95     | .750               | 18.50    | 6.08      | .920               | 7.000 |
| 4.54     | .780               | 19.76    | 5.66      | .972               | 6.632 |
| 4.77     | .420               | 19.60    | 5.93      | .522               | 6.452 |
| Average  |                    |          |           |                    |       |
| 4.67     | .653               | 19.17    | 5.77      | .808               | 6.578 |

100 parts pentosan in the corn kernel consist of 87.72 parts pentosan and 12.28 parts methyl pentosan.

Botanically seen, the corn kernel is a one-seeded, dry, indehiscent fruit (caryopsis). Pericarp and testa grow together forming the hulls. Inside the hulls is endosperm and embryo. The former consists of parenchym cells containing starch granules or starch and gluten granules together and in its periphery one single layer of cells: the enzyme cells (aleurone cells).

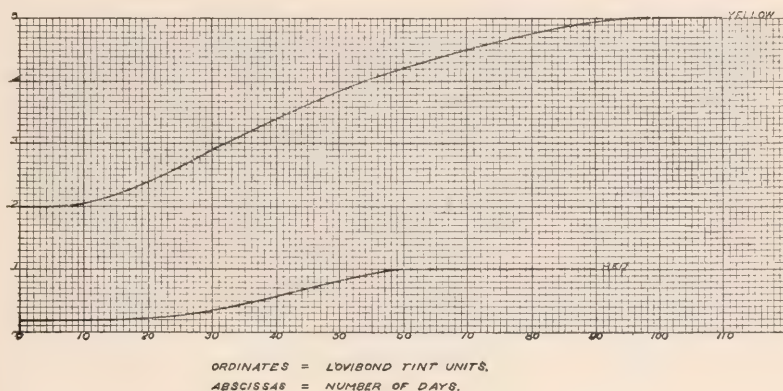
The enzyme cells do not contain starch but chiefly fat and protein. They cover that part of the endosperm which contains "horny starch."

On the upper side of the corn kernel, between hulls and endosperm and submerged in this latter we find the embryo (germ) consisting of the large scutellum with embryo root, stem and bud.

The grade of corn used generally in the corn products industry consists of

2.
  - 6.8% hulls
  - 85.7% endosperm
  - 7.5% germ.

## 80 SUGAR.

25% SOLUTION IN  $\frac{1}{2}$ " CELL, LOVIBOND'S COLORIMETER.

To test what amount of pentosans these various component parts of the corn contained, a disintegration was made in the following way: Corn was steeped in boiling water for a few seconds, then hulls and germ were easily removed from the endosperm with a penknife.

I tried to separate the enzyme cells from the rest of the endosperm but did not succeed in getting a clean preparation, as it was impossible to skin off this layer of cells without getting some of the starchy endosperm removed too. Instead I made a preparation of endosperm from which all of the enzyme cells were removed.

These four preparations gave the following results:

|                                 | Pentosan | Methyl<br>Pentosan | 100 parts Pentosan consist of<br>Tptal | Pentosan | Methyl<br>Pentosan |
|---------------------------------|----------|--------------------|--|----------|--------------------|
| Hulls                           | 48.620%  | 6.040%             | 54.660%                                | 88.95    | 11.05              |
| Endosperm                       | 1.690%   | .867%              | 2.557%                                 | 66.09    | 33.91              |
| Endosperm<br>minus enzyme cells | .422%    | 1.130%             | 1.552%                                 | 27.19    | 72.81              |
| Germ                            | 8.382%   | .231%              | 8.613%                                 | 97.32    | 2.68               |

From the above data it is very interesting to notice that the enzyme cells must be very rich in pentosans, since the removal of



this relatively small percentage of the endosperm brings the total percentage of pentosans down from 2.557 to 1.552.

It is also interesting to see how comparatively rich the endosperm and especially the starchy part of the endosperm is in methyl pentosans. Applying the results in Table 3 to the results in Table 2, I find that the component parts of 100 gram, dry corn contain:

|              | Pentosan | Methyl Pentosan | Total |
|--------------|----------|-----------------|-------|
| 4. Endosperm | 1.45     | .74             | 2.19  |
| Hulls        | 3.31     | .41             | 3.72  |
| Germ         | .63      | .02             | .65   |
|              | <hr/>    | <hr/>           | <hr/> |
| Total        | 5.39     | 1.17            | 6.56  |

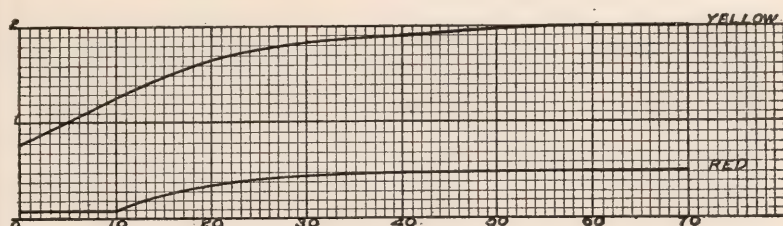
The disintegration of the corn on a factory scale is performed by soaking the corn with lukewarm water to which a small amount of sulphurous acid has been added until it is sufficiently softened for the milling process; then it is separated from the water and cracked in steel mills. The germ can now be separated by mechanical means; it is dried and ground into germ meal containing about 55% oil, most of which is removed by pressing, leaving as a residue the corn oil cake still containing about 10% oil. On a manufacturing scale it is naturally impossible to free the germ from particles of endosperm and especially hulls; furthermore it must be remembered that a great part of the organic phosphates and other extractive matter largely present in the germ has been removed during the steeping process, consequently I find a higher amount of pentosans present in factory samples than in laboratory-prepared samples.

Average analysis showed the following results:

|              | Pentosan | Methyl Pentosan | 100 parts Pentosan consist of |          |                 |
|--------------|----------|-----------------|-------------------------------|----------|-----------------|
|              |          |                 | Total                         | Pentosan | Methyl Pentosan |
| 5. Germ meal | 11.43    | .570            | 12.000                        | 95.25    | 4.75            |
| Oil cake     | 23.00    | .852            | 23.852                        | 96.43    | 3.57            |

After separation of the germ the rest of the corn is ground in buhr mills. The ground material is run over silk sieves which

## 70 SUGAR

25% SOLUTION IN  $\frac{1}{2}$ " CELL, LOVIBOND'S GOLDMETER

ORDINATES = LOVIBOND TINT UNITS

ABSCISSAS = DAYS

separate the hulls from the liquid containing starch and gluten. This liquid runs over tables where most of the starch, called "green starch," settles while the gluten runs away with the tailings.

A part of this gluten which still contains 30 to 40% starch on dry basis is concentrated, filter-pressed and dried. This product is known as gluten meal.

The other part of the gluten liquor is mixed with the hulls, filter-pressed and dried together with the concentrated corn soluble, extracted during the steeping process. This product is known as gluten feed.

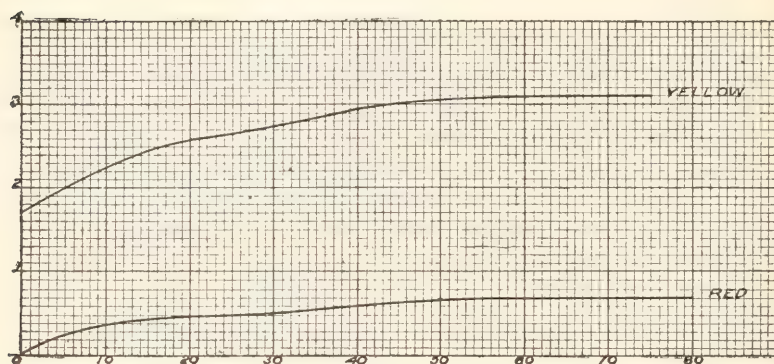
The following table gives the average analyses of these various products:

| 6.           | 100 parts total Pentosan consist of |                 |       |          |                 |
|--------------|-------------------------------------|-----------------|-------|----------|-----------------|
|              | Pentosan                            | Methyl Pentosan | Total | Pentosan | Methyl Pentosan |
| Gluten Meal  | 4.06                                | .496            | 4.556 | 89.11    | 10.89           |
| Hulls        | 39.96                               | 2.790           | 42.75 | 93.47    | 6.53            |
| Corn Soluble | 1.74                                | .462            | 2.202 | 79.02    | 20.98           |
| Gluten Feed  | 18.58                               | 1.21            | 19.79 | 93.89    | 6.11            |
| Green Starch | .98                                 | 1.40            | 2.38  | 41.28    | 58.82           |

The corn soluble gives by the distillation furfural corresponding

## CORN SYRUP (UNDILUTED)

6" CELL, LOVIBOND'S COLORIMETER.



ORDINATES = LOVIBOND TINT UNITS

ABSCISSAS = DAYS

to 2.202% pentosans, showing that the corn either contained pentoses which are extracted or that hydrolysis of pentosans has taken place in the steeping process. Before the green starch is used for food purposes it is washed first with weak solution of caustic soda and then several times with water; after each washing the starch is passed over silk sieves.

Average analysis of food starches:

| 7.       |                 |       | 100 parts total Pentosan consist of |                 |
|----------|-----------------|-------|-------------------------------------|-----------------|
| Pentosan | Methyl Pentosan | Total | Pentosan                            | Methyl Pentosan |
| .48      | 1.21            | 1.69  | 28.4                                | 71.6            |

It will be seen from these results that even a very careful washing and sifting does not remove pentosans from the starch.

## REFINERY PRODUCTS

These are the acid hydrolyzed products of corn starch either in syrup form—as corn syrup—or in form of crystallized glucose with more or less moisture content.

As we have seen, it is practically impossible to prepare corn starch free from pentosans, consequently we may expect to find

small amounts of pentosan hydrolyzation products in the various refinery products, and, as an ultimate product of the hydrolyzation, furfural.

Table 8 shows the percentage of pentosans present in starch used for the hydrolysis, and the amount of pentosan hydrolyzation products in the finished corn syrup and corn sugars which yield furfural by Tollens method. All results are given as pentosan and methyl pentosan, an absolutely dry basis.

| 8.   | 100 parts total Pentosan consist of |                 |       |          |                 |
|--|-------------------------------------|-----------------|-------|----------|-----------------|
|  | Pentosan                            | Methyl Pentosan | Total | Pentosan | Methyl Pentosan |
| Starch used for Corn Syrup                         | .623                                | 1.26            | 1.883 | 33.09    | 66.91           |
| Corn Syrup (42% Glucose on dry basis)              | .776                                | .897            | 1.673 | 46.38    | 53.62           |
| Anhydrous Sugar (97% Glucose on dry basis)         | .722                                | 1.18            | 1.902 | 37.96    | 62.04           |
| Bread sugar (94½% Glucose on dry basis)            | .656                                | .980            | 1.636 | 40.10    | 59.90           |
| Hydrol (is the mother liquor from the bread sugar) | .860                                | 1.79            | 2.650 | 32.45    | 67.55           |
| Starch used for (80 and 70 sugars)                 | .649                                | 1.24            | 1.889 | 34.36    | 65.64           |
| 80 Sugar (92% Glucose dry basis)                   | .68                                 | 1.06            | 1.740 | 39.08    | 60.92           |
| 70 Sugar (86½% Glucose dry basis)                  | .72                                 | 1.15            | 1.870 | 38.50    | 61.50           |

Every manufacturer of products of starch hydrolysis has noticed the more or less rapid colorization of syrup and sugars when these are stored for some time. The 3 sets of curves accompanying this paper show the rate of colorization in corn syrup, 80 and 70 sugar.

The ordinates indicate the units of the composing red and yellow colors according to Lovebond's standard and the abscissas indicate the number of days of storing under ordinary warehouse conditions.

The corn syrup was examined undiluted in a 6'' cell while the sugars were dissolved to a 25% solution and examined in a ½'' cell.

It will be seen that the curves after a certain number of days run parallel with the abscissas, showing that the color increase ceased.

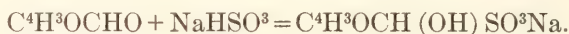
It is undoubtedly a slow oxidation that has taken place here; addition of reducing agents to corn syrup and sugars, as for instance



sulphurous acid in the form of bisulphites, will check the color increase. As furfural may be considered as an ultimate product formed by the acid hydrolyzation of pentosans there is a possibility of its presence in hydrolyzation products of corn starch, and as furfural rapidly changes from a colorless solution when freshly prepared into a dark brown solution, when exposed to the air, we may draw the conclusion that the slow color increase of refinery products is due chiefly to the presence of traces of furfural. To comply with the pure food law, American manufacturers have abandoned the use of sulphites for preserving the color of corn syrup and sugars, but manufacturers in other countries use it as a general rule.

That sulphites check the colorization of furfural in corn syrup was shown by the following experiment:

To samples of corn syrup, which after storing showed a very slight but constant color, were added small percentages of furfural and to other samples the same amount and equivalent amounts of sodium bisulphite according to the reaction.



While the first series of samples showed a gradual increase of color the other series remained unchanged, retaining the same color as the original sample.

There is still another possibility for color increase which I shall mention here. The refinery starch will always contain traces of protein—about .05% nitrogen; while we are able to trace nearly all the pentosans in the starch down to the various refinery products, only very small amounts of nitrogeneous matter can be found here—corn syrup, for instance, containing only from .005 to .01%. But when the protein molecule is broken up during the conversion, traces of oxybenzoles or derivates of oxybenzoles may be formed, and it is a well-known fact that furfural, in connection with oxybenzoles, forms products of very pronounced colors.



## RESEARCH ON LINTNER'S POLARIMETRIC METHOD FOR THE DETERMINATION OF STARCH

BY CHRISTIAN E. G. PORST AND HARRY A. CROWN

*Coytesville, N. J.*

Desiring a quicker and more accurate method than the diastase method for the determination of starch in corn and corn products, the authors decided to investigate Lintner's polarimetric method, which appeared to be promising, to see if it were applicable to corn products. It was therefore necessary to try it out under various conditions to establish its reliability.

The greatest source of error is the hydrolyzation or partial hydrolyzation of the starch by the concentrated acid. Therefore the authors made a study on a pure corn starch under various conditions to determine those under which hydrolyzation is minimum or constant.

Several tests were made with weights of starch varying from 0.1 gram to 15 grams but the readings were not exact multiples of the various weights, therefore 5 grams were arbitrarily chosen. Readings were made in a Schmidt and Hänsch half-shadow polariscope with triple field of vision, in a 200 mm. tube and expressed in degrees Ventzke.

When water is added to starch, there is an elevation of the temperature and when concentrated hydrochloric acid is added to the mixture, the temperature rises still more, due to the heat of dilution of the acid and an exothermic reaction between the starch and the acid. Therefore it was found necessary to cool down the starch and water mixture and to keep the hydrochloric acid in a freezing mixture. The following test made roughly will show the heat effects:

Fifteen grams pure starch, 50 cc. water and 100 cc. concentrated HCl were cooled down in separate beakers. The water was added to the starch, to which the hydrochloric acid was then added.

Temperature of starch =  $14.1^{\circ}$  C.

Mixture =  $16.5^{\circ}$  C.

Temperature of water =  $14.0^{\circ}$  C.

Temperature of HCl =  $10.0^{\circ}$  C.

Mixture starch }  
Water and acid } =  $29.4^{\circ}$  C.

1. *Effect of Varying the Temperature of Steeping with Concentrated HCl.*

Weight of starch taken, 5 gms.; time of steeping, 30 minutes; time of standing after steeping to time of reading, 45 minutes.

All temperatures were brought to  $20^{\circ}$  C. immediately after steeping.

| Temperature<br>HCl | Temperature<br>Starch water HCl | Temperature<br>during the<br>30 min steep. | Reading           |
|--------------------|---------------------------------|--|-------------------|
| $3.5^{\circ}$ C.   | $14.2^{\circ}$ C.               | $5^{\circ}$ C.                             | $26.7^{\circ}$ C. |
|                    | $13.2^{\circ}$ C.               | $5^{\circ}$ C.                             | $26.6^{\circ}$ C. |
|                    | $12.2^{\circ}$ C.               | $10^{\circ}$ C.                            | $26.3^{\circ}$ C. |
| $2.0^{\circ}$ C.   | $12.5^{\circ}$ C.               | $10^{\circ}$ C.                            | $26.3^{\circ}$ C. |
| $2.6^{\circ}$ C.   | $8.0^{\circ}$ C.                | $10^{\circ}$ C.                            | $26.4^{\circ}$ C. |
| $1.0^{\circ}$ C.   | $12.2^{\circ}$ C.               | $15^{\circ}$ C.                            | $26.3^{\circ}$ C. |
| $2.0^{\circ}$ C.   | $12.5^{\circ}$ C.               | $15^{\circ}$ C.                            | $26.3^{\circ}$ C. |
| $0^{\circ}$ C.     | $12.8^{\circ}$ C.               | $15^{\circ}$ C.                            | $26.3^{\circ}$ C. |
| $3.2^{\circ}$ C.   | $18.8^{\circ}$ C.               | $20^{\circ}$ C.                            | $26.0^{\circ}$ C. |
| $0.6^{\circ}$ C.   | $20.0^{\circ}$ C.               | $20^{\circ}$ C.                            | $26.0^{\circ}$ C. |
| $2.7^{\circ}$ C.   | $18.8^{\circ}$ C.               | $20^{\circ}$ C.                            | $26.0^{\circ}$ C. |
| $3.5^{\circ}$ C.   | $18.4^{\circ}$ C.               | $25^{\circ}$ C.                            | $25.6^{\circ}$ C. |
| $4.0^{\circ}$ C.   | $19.0^{\circ}$ C.               | $25^{\circ}$ C.                            | $25.6^{\circ}$ C. |
| $3.0^{\circ}$ C.   | $20.5^{\circ}$ C.               | $25^{\circ}$ C.                            | $25.6^{\circ}$ C. |

It is evident that the hydrolysis is less at the lower temperatures, but, due to the exothermic reactions, it would not be practicable to work at those temperatures. Twenty degrees Centigrade has been found to be the most convenient temperature.

2. *Time of Steep Variable.*

Weight starch, 5 gms.; temperature of steep,  $20^{\circ}$  C.

Time of standing after steeping to time of reading was made 45 minutes.

| Temperature<br>HCl | Temperature<br>Mixture | Time of steeping<br>with conc. HCl | Reading   |
|--------------------|------------------------|------------------------------------|-----------|
| 6.0° C.            | 17.3° C.               | 5 min.                             | 25.8° C.  |
| 3.1° C.            | 16.4° C.               | 10 min.                            | 26.3° C.  |
| 5.0° C.            | 14.5° C.               | 15 min.                            | 26.3° C.  |
| 3.5° C.            | 16.3° C.               | 20 min.                            | 25.9° C.  |
| 5.0° C.            | 14.6° C.               | 25 min.                            | 25.95° C. |
| 2.9° C.            | 24.5° C.               | 35 min.                            | 25.7° C.  |
| 6.4° C.            | 24.6° C.               | 40 min.                            | 25.6° C.  |

We found that steeping for five minutes is not sufficient for all the starch to go into solution. After reaching the maximum, the readings decrease with increase in time of steeping.

3. *Time of Standing after Adding Phosphotungstic Acid until Reading is Taken, Variable.*

Weight starch, 5 gms.; temperature of steep, 20.° C.; time of steep, 30 minutes.

| Time of<br>Standing | Reading | Time of<br>Standing | Reading | Time of<br>Standing | Reading |
|---------------------|---------|---------------------|---------|---------------------|---------|
| $\frac{1}{2}$ hour  | 26.2    | 3 hrs. 11 min.      | 25.6    | 5 hrs. 4 min.       | 25.4    |
| $\frac{1}{2}$ hour  | 26.2    | 3 hrs. 15 min.      | 25.5    | 5 hrs. 7 min.       | 25.3    |
| 1 hour              | 25.8    | 3 hrs. 13 min.      | 25.6    | 5 hrs. 7 min.       | 25.3    |
| 1 hour              | 25.8    | 3 hrs. 26 min.      | 25.4    | 5 hrs. 6 min.       | 25.2    |

The hydrolyzation of the starch increases as the time of standing continues. However, it seems to be constant for a given time of standing. The change is greater during the first three hours than during the subsequent two.

4. The following set was run with the time of standing, until the reading was taken, constant at 45 minutes. After steeping, the phosphotungstic acid was added and the solution made up to 200 cc. with hydrochloric acid of 1.125 specific gravity and allowed to stand 30 minutes in a water bath kept at 20.° C. Then it was filtered, and exactly 15 minutes later the reading was taken.

Weight starch, 5 gms.; temperature of steep, 20.° C.; time of steep, 30 minutes; time of standing to reading, 45 minutes.

| Temperature<br>HCl | Temperature<br>Mixture | Reading   |
|--------------------|------------------------|-----------|
| 2.4° C.            | 20.8° C.               | 26.0° C.  |
| 2.4° C.            | 22.6° C.               | 26.0° C.  |
| 2.7° C.            | 21.7° C.               | 26.0° C.  |
| 1.5° C.            | 20.2° C.               | 26.0° C.  |
| 0.5° C.            |                        | 26.05° C. |

5. In all the preceding cases, 10 cc. of a 4% water solution of phosphotungstic acid were used. In the following set, the amount was varied, other conditions being constant. The required amount of a 20% solution was made up with water to 10 cc. and then added to the starch solution.

Weight starch, 5 gms; temperature of steep, 20° C.; time of steep, 30 minutes; time of standing from steep to reading, 45 minutes.

| Amount of Phosphotungstic Acid                 | Reading  |
|--|----------|
| nil  | 26.3° C. |
| 5 cc. of 4% solution                           | 26.1° C. |
| 5 cc. of 4% solution                           | 26.1° C. |
| 3 cc. of 20% solution equivalent to 15 cc. 4%  | 25.6° C. |
| 4 cc. of 20% solution equivalent to 20 cc. 4%  | 25.3° C. |
| 5 cc. of 20% solution equivalent to 25 cc. 4%  | 25.1° C. |
| 6 cc. of 20% solution equivalent to 30 cc. 4%  | 24.8° C. |
| 7 cc. of 20% solution equivalent to 35 cc. 4%  | 24.9° C. |
| 8 cc. of 20% solution equivalent to 40 cc. 4%  | 24.6° C. |
| 9 cc. of 20% solution equivalent to 45 cc. 4%  | 24.4° C. |
| 10 cc. of 20% solution equivalent to 50 cc. 4% | 24.4° C. |

The white hydrated tungstic acid was precipitated in each flask containing the equivalent of 15 cc. or more of a 4% phosphotungstic acid solution, increasing in volume with the amount of phosphotungstic acid added. Some starch was also thrown down, since the reading diminishes with increase in phosphotungstic acid.

Many other determinations were made on the same pure starch with all conditions constant.

Weight starch, 5 gms.; time of steep, 30 minutes; temperature, 20.° C.; time of standing from steep to reading, 45 minutes; amount of phosphotungstic acid, 10 cc. of 4% solution.

In all, the readings were 26.0° V. From this value the specific rotatory power of dry corn starch was computed to be 199.413°, the moisture in the starch being 10.038%.

Observing the conditions of time and temperature, the method will read as follows:

Five gms. of starch, or a weight of the finely ground substance equivalent to 5 gms. starch, are mixed with 20 cc. of water in a mortar, cooled down in ice water. To this is added 40 cc. concentrated HCl previously cooled down in a freezing mixture, and then the solution is kept at 20.° C. for  $\frac{1}{2}$  hour. The contents of the mortar are then transferred to a 200 cc. flask, 10 cc. of a 4% phosphotungstic acid solution added, and made up to the mark at 20.° C. with HCl of 1.125 specific gravity. The flask is then kept for  $\frac{1}{2}$  hour in a water bath at 20.° C., filtered and, exactly 15 minutes after filtering, the reading is taken at 20.° C.

The method was now applied to the determination of the starch in the corn kernels. Many determinations were made taking 7 grams of the ground corn in work and the readings checked well. A correction for the water solubles was made by taking an aliquot part of the water solution representing 7 grams original sample, and subtracting this from the readings obtained for the corn.

The diastase method was used for comparison.

Starch in the corn on dry basis, Lintner's method — 68.62%.

Starch in the corn on dry basis, diastase method — 68.54%.

A sample of an intermediate product, obtained in the manufacture of corn products from the disintegrated maize kernels consisting chiefly of hulls with some adhering starch from the endosperm, was tried and compared with the diastase method, the results checking well.

Lintner's method — 17.2% starch on dry basis.

Diastase method — 17.3% starch on dry basis.

The authors next desired to test the method with a product high in protein content and so took samples of gluten meal, which is a product very rich in gluten (protein from 40 to 50%). It was found that the polarimetric readings increased with the amount



of phosphotungstic acid which precipitates the protein. The maximum reading was obtained when 10 cc. of a 20% solution, equivalent to 50 cc. of a 4% solution, were used. Then, as more phosphotungstic acid was added, the readings gradually became lower, due to the precipitation of some starch, as we have shown in Table No. 5.

The percentage of starch on dry basis corresponding to the maximum reading was 44.7%.

Sachsse's method gave 45.2%.

#### CONCLUSIONS

1. Results are concordant when the same conditions are observed.
2. The method checks fairly well with the diastase and Sachsse methods.
3. It is rapid, taking only 1 hour and 15 minutes.
4. Results are evidently too low when an excess of protein is present.
5. The worker is not troubled by HCl fumes when the temperature is kept at 20.° C.

## BAMBOO CELLULOSE

BY WILLIAM RAITT, F. C. S., CELLULOSE EXPERT

*Attached Imperial Forest Research Institute, Dehra Dun, U. P.  
India*

1. In this paper is given a condensed account of the results of an enquiry into the cellulose yielding possibilities of Indian bamboos. Any one desirous of following up the investigation in its full details is recommended to obtain Part III of Vol. III of "The Indian Forest Records" which will shortly be published by the Superintendent, Government Printing, Calcutta, and which will contain the official report of the enquiry.

2. A survey of the research work already accomplished by Sindall, Richmond and others, and of detailed reports of a number of large-scale factory tests made in India and England resulted in the preparation of a "present position" statement as follows:

a. A general agreement as to the suitability of bamboo cellulose for the manufacture of paper, and especially of printing and litho grades, provided its isolation has been successfully accomplished.

b. A general agreement that reduction by soda is the only practical method applicable and that the bi-sulphite process is unsuitable.

c. A general agreement that the nodes are irreducible within practical cost limits and that they must be cut out and rejected.

d. In regard to internodes a great divergence of opinion and statement as to the practical results obtained, soda consumption varying from 16 to 40%, bleaching powder from 9 to 40% and cellulose yield from 33 to 50%. Some experimentalists claim even and regular digestion, while others assert that the results are irregular and frequently spoilt by the presence of hard and imperfectly digested matter.

It was resolved that the present investigation, while taking full advantage of all that had previously been done and reported, should concern itself specially, 1st, with the points upon which

opinion and results varied, in an attempt either to reconcile the divergencies or to eliminate their causes, and 2nd, in an endeavour to utilise the nodes, it being recognised that their rejection constitutes a serious drawback to the successful exploitation of bamboo, not merely in the waste of from 7 to 15% of raw material but also in the troublesome and costly nature of the cutting-out process owing to the destructive effect of the siliceous cuticle on steel cutting edges.

3. Previous workers in this field have laboured under serious disadvantages on account of the little that was known of bamboo economics. Hitherto regarded as a more or less waste and worthless jungle product, scarcely any attention has been given to the collection of information dealing with its commercial exploitation on a large scale. The bearing of this state of ignorance upon the causes of the divergent opinions and results referred to above is obvious. It might be the case that some of these were due to peculiarities of species which were of no commercial importance. With species numbering some hundreds growing over a wide range and variety of latitude, elevation, climate and soil, it would not be surprising if a considerable difference in results should occur. It did therefore appear that a necessary preliminary to this investigation must be a systematic enquiry into the exploitation economics of bamboo.

4. Such an enquiry was duly instituted and carried out by Mr. R. S. Pearson of the Indian Forest Service, official Forest Economist to the Government of India. His report came to the somewhat surprising, but perfectly well founded, conclusion that out of the many species available in India and Burma only five, *viz.*, *Bambusa Tulda*, *B. arundinacea*, *B. polymorpha*, *Cephalostachyum pergamile* and *Melocanna bambusoides*, exist in commercial quantities and under economically exploitable conditions. Though few in number these species are each so dominant in their own areas that they probably represent 80% of the whole growing stand of bamboo in the country, and it is somewhat remarkable that they are the sorts that have hitherto proved easiest to treat and that several of those which have been excluded do present difficulties, peculiar to themselves, sufficient to account for some of the contradictory results which have been recorded.

But while thus limiting and simplifying the problems before the experimenter, Mr. Pearson's report did introduce a new difficulty which we had not anticipated. We have hitherto paid considerable attention to bamboo as a plant whose resistance to reduction increased with age and much time and effort has been expended on the establishment of degrees of treatment suitable for various ages. Now we learn that all this has been wasted and useless labour for the simple reason that in large-scale forest exploitation, differentiation as to age is impossible, that there are no indications whatever enabling one to distinguish between 2, 3, 4 or 5 year old stems and that even in the case of yearling culms their slight difference of appearance disappears after a few weeks' drying. In short, we must deal with bamboo of all ages, mixed and as a whole or not at all, and all we can hope to do in the way of selection is to keep species separate.

5. A short experience of bamboo digestion enables us to suggest the following as being among the more obvious reasons for its difficulties and for the irregularity and imperfection in the results:—

a. Its tendency to float, permitting a portion of the digester charge to be buoyed up out of contact with the liquor for a considerable time.

b. Its resistance to liquor penetration and the variation of this in accordance with the size of the chip, small chips digesting more quickly and more perfectly than large ones. Also the variation in this respect in accordance with age, a charge of mixed age being invariably irregularly digested.

An examination of its structural, physical and microscopic features yielded the following results:—

6. *Specific Gravity.* A bamboo culm is light and bouyant solely because it is hollow. Its component wood is really as heavy as many of our commercial hardwoods. Its actual specific gravity varies somewhat with species, that of the lightest of the five species we are concerned with being .8410 for internodes and .8091 for nodes, while the heaviest is .9555 internodes, and .9170 nodes. These results are on two year old samples but the figures do not appreciably vary with age after maturity (one year) has been reached. It is important to note that nodes are actually



lighter than internodes, therefore their greater resistance to digestion is not due to greater density. Bamboo is therefore of about twice the specific gravity of the common pulp woods, spruce and fir, a fact which, when realised in all its bearings, throws considerable doubt to whether we have been right in treating it on similar lines as to wood so far as its preliminary preparation for digestion is concerned.

7. *Capillary Air.* A marked microscopic feature of bamboo is the sap canals or vessels of comparatively large size and visible with a low power lens. They appear in groups of four arranged in the form of rhomboid squares. The groups are about 1 mm. distant from each other, and in the groups the tubes are about 0.5 m.m. apart. Their diameter is 0.1 m.m., mostly circular in shape though occasionally one of oval contour is found. In a bamboo of 3 inches' diameter with walls half an inch thick there are about 8000 of them. They run in continuous and uninterrupted parallel series throughout the whole length of the culm and are not broken at the nodes but merely slightly displaced from the true parallel and vertical direction. They do not collapse in drying but retain their full size and shape and consequently their air-carrying capacity. Dry bamboo is therefore largely impregnated with air in a state of capillarity, a condition which makes it somewhat difficult to expel and which fully accounts for the tendency to float which is one of the chief difficulties in its digestion. When a mass of bamboo chips is boiled in an open vessel and prevented from floating by being held under the water surface, the expelled air forms a dense dome of froth over the water. Spruce chips similarly dealt with throw up a few air bubbles only. When not prevented from floating, bamboo floats considerably longer than spruce in spite of its greater specific gravity. The greater lightness of spruce permits a much larger proportion of its mass to be buoyed up out of contact with the water, but the whole of the buoyed portion sinks under the surface much sooner than the smaller buoyed portion of bamboo. The capillary air in the latter resists soakage longer and it cannot wholly sink until this has been expelled and its place taken by water. In an experiment made with equal quantities of bamboo and spruce chips, thrown into open vessels containing equal volumes of NaOH



liquor, and boiled, the spruce took one hour to wholly sink while the bamboo required two and a half hours. When forcibly sunk and held under the surface by a perforated plate and then boiled, it continues to throw up air bubbles for two hours. It is not difficult to appreciate the light which this throws upon some of the digestion failures of the past and it supplies another reason for doubt as to whether we have been justified in basing our treatment of bamboo upon our experience with wood.

8. *Structural Resistance.* Here again we find conditions differing totally from those of spruce which is almost equally resistant in all directions to mechanical disintegration, but being a soft wood of low specific gravity it has little mass resistance to the soakage and penetration of liquor. Bamboo is a hard and heavy material but is strongly resistant to mechanical force in the transverse direction only. To a splitting or crushing force acting longitudinally, it has scarcely any resistance whatever and it is possible by careful dissection to isolate individual filaments or fibre bundles and to follow them up along the nodes and through the internodes for the whole length of the culm. It is this facility of separation of its fibrous structure and absence of interlacing with adjoining filaments, together with the large interior surface of the sap canals exposed to chemical action (provided the air is expelled), which permits us to remove it from the category of impervious hard woods in which its high specific gravity and transverse hardness would otherwise place it. But, in chips, with its transverse hardness not destroyed and its capillary air not expelled, it presents a mass resistance to the penetration of solvents immensely greater than spruce.

9. A physical and microscopical examination therefore leads to the following conclusions, *viz.*, that the digestion difficulties are to a considerable extent due to:—

a. A mass or structural resistance to penetration of liquor varying with the size of the individual chip, therefore the smaller the particles and the more regular their size the better will be the results.

b. The resistance of the capillary air. If this could be expelled prior to digestion so that the liquor would be free to at once attack the interior of the sap vessels, the benefit would no doubt be great.

It is also clear that the greater difficulties presented by both the nodes and the older internodes is not due to greater density. An explanation of it must be sought in their chemical composition.

10. The scheme of analysis adopted is based wholly on the varying solubilities of the component substances as follows:

Group I. Matter soluble in water at 100°C., chiefly starch and its transformation products, with colouring matter and soluble salts.

Group II. Matter soluble in 1% NaOH at 100°C., chiefly pectose with small quantities of fat and wax. (When isolated by hot ether-alcohol treatment the latter varies in amount with species from 0.75 to 1.70%. Resides chiefly in the cuticle.)

Group III. Lignin, soluble only in strong NaOH at temperatures above 130 C.

Group IV. Cellulose, the insoluble residue from the sodium hydroxide-chlorine-sodium sulphite treatment of Messrs. Cross and Bevan.

Ash is not included in the percentage proportions because each of the above groups carries out with it its own complement of silica or salts or both. To include it would therefore have the effect of reckoning it twice. *Hydroscopic moisture* is also excluded, all the determinations being made on the absolutely dry substance. The following on dry seasoned *B. polymorpha* is typical of all the species mentioned except *Melocanna B.* which has more lignin and less pectose. The whole culm sample taken contained both nodal and internodal substances in their strict proportions as they exist in a whole culm.

|                      | WHOLE CULM                           |                    |                     |                       |                          |                                    |
|----------------------|--------------------------------------|--------------------|---------------------|-----------------------|--------------------------|------------------------------------|
|                      | Young<br>culm<br>$\frac{3}{4}$ grown | One<br>year<br>old | Two<br>years<br>old | Three<br>years<br>old | Nodes<br>only<br>2 years | Inter-<br>nodes<br>only<br>2 years |
| G. I. Starch, etc.   | 13.10                                | 11.60              | 8.95                | 6.90                  | 9.83                     | 8.70                               |
| G. II. Pectose, etc. | 25.23                                | 19.02              | 20.60               | 22.52                 | 26.44                    | 20.19                              |
| G. III. Lignin       | 5.62                                 | 15.66              | 15.74               | 15.96                 | 17.60                    | 15.29                              |
| Cellulose            | 56.05                                | 53.72              | 54.71               | 54.62                 | 46.13                    | 55.82                              |
|                      | 100.00                               | 100.00             | 100.00              | 100.00                | 100.00                   | 100.00                             |
| Ash                  | 2.61                                 | 4.73               | 3.97                | 2.18                  | 4.50                     | 3.87                               |

The analyses may be interpreted thus:—lignification begins with the sprouting of the branches which occurs when the culm is three-fourths grown and is complete at one year old, little or no change in this respect happening afterwards. At the half-grown stage the plant is wholly pecto-cellulose in character. With the rapid increase in lignin at maturity there is a corresponding reduction in pectose, but with advancing age a gradual increase in the latter at the expense of the starch group.

Nodes compared with internodes show a large increase in pectose and rather more lignin.

11. The plant is distinctly of a pecto-ligno-cellulose character, having both pectose and lignin in considerable quantity and thereby differing seriously from any other material in common use. I have determined the effects of the three groups of solubles upon soda consumption to be approximately as follows:

Group I combines with 0.22 for each 1% in the analysis.

Group II combines with 0.32 for each 1% in the analysis.

Group III combines with 0.66 for each 1% in the analysis.

These figures are for complete but *bare* digestion only, under suitable conditions of time and temperature, and do not take into account any excess of NaOH which it may be advisable to use to obtain a bleaching effect. If we now calculate the quantity of soda required for one and three year old in accordance with the above figures we get:

| 1 year old at NaOH                    |                      | 3 year old at NaOH   |              |
|---------------------------------------|----------------------|----------------------|--------------|
| Gr. I                                 | 11.60 c 0.22 = 2.55  | 6.90 c 0.22 = 1.52   |              |
| Gr. II                                | 19.02 c 0.32 = 6.09  | 22.52 c 0.32 = 7.21  |              |
| Gr. III                               | 15.66 c 0.66 = 10.34 | 15.96 c 0.66 = 10.53 |              |
| Add $\frac{1}{2}$ per cent excess     | <u>.50</u>           |                      | <u>.50</u>   |
| Per cent required on dry raw material |                      |                      |              |
|                                       | <u>19.48</u>         |                      | <u>19.76</u> |
| Per cent on air dry                   |                      |                      |              |
|                                       | <u>17.54</u>         |                      | <u>17.79</u> |

Similarly on the node and internode analysis we get a theoretical consumption for the latter of 17.07% and for the former 20.47%. Three year old ought therefore to digest satisfactorily with the same consumption of NaOH as one year old, and nodes with  $3\frac{1}{2}\%$

more than internodes. What actually occurs is this: in one year old the internodal chips are fairly well digested but the nodal chips are not; in three year old, internodal chips are badly digested and nodal ones scarcely softened. Internode chips digested by themselves with 17% yield good results but node chips by themselves will not digest with even 30%. But, if instead of dealing with the material in chips we reduce it by *crushing* to an extremely fine state of sub-division of filaments, the whole difficulty disappears at once. A whole stem, nodes included, when suitably crushed will digest satisfactorily with the theoretical  $17\frac{1}{2}$  or 18% of NaOH and it makes no difference whether it is one or three year old, and in the product there is absolutely no indication whatever of the nodes. All good pulp and no chips.

12. We have already seen (paragraph 9) that the greater resistance of old bamboo and especially of nodes is not due to greater density. Neither can we attribute it to capillary air which can only delay and not prevent digestion and, in any case, there is no difference in this respect noticeable between old and young stems or between nodes and internodes. The only variation remaining which can have any effect is in the *pectose* contents which are  $5\frac{1}{4}$ % greater in three year old than in one, and 6% more in nodes than internodes. But, as shown by the soda estimates (in paragraph 11), these increases do not call for any greater consumption in the case of three year old and for only  $3\frac{1}{2}$ % more for nodes. I therefore hazard the hypothesis that the secret of the whole trouble lies in the greater physical resistance to liquor penetration created by the larger and thicker masses or films of pectose matter in which the filaments of the nodes and older internodes are buried. When we consider that under the normal conditions of digestion, *viz.*, high temperature and strong NaOH, pectose *gelatinises*, it does not appear impossible to imagine a colloidal resistance set up similar to that which occurs on the surface of a lump of resin when thrown into boiling NaOH, or upon a cake of gelatine when put into hot water. Such a colloidal result would exercise a protective effect upon the lignin, especially in the interior of a chip where the colloidal films or masses and the matter which they enclosed would be more or less imprisoned and hindered from floating away freely in the liquor. But *crushing*



counteracts this imprisonment, and by reducing the pectose masses and films from large to small and thick to thin and destroying their mere physical cohesion, the colloidal resistance is reduced in a similar manner to that of the lump of resin above referred to when it is crushed to powder and in that condition added to the boiling NaOH. The immensely greater surface area presented to the action of the liquor by the fine particles prevents a colloidal effect being established. Any how, whatever may be the true reason, the fact remains that crushing solves the difficulty, not only as regards mixed ages, but also that of the nodes, and the whole bamboo can now be digested with no more (or very slightly more) than its theoretical quantity of soda and at a lower temperature and in a shorter time than in the case of chips with nodes excluded.

13. Crushing, when thoroughly done, reduces the whole bamboo to soft fibrous masses something like hanks of coarse tow and with its original brittleness largely destroyed. The distinctive appearance of the nodes is lost, it being difficult to tell, in the crushed mass, which is node or internode. This result is largely aided by the structural features mentioned in paragraphs 7 and 8. The crushing fracture runs along the groups of capillary tubes which form weak places in the wall and which split open. The capillary air trouble is thus got rid of and the interior of the tubes opened up to immediate attack by the liquor. This means that the floating trouble is got rid of and the period of digestion reduced. So completely is the air resistance destroyed that the sp. gr. of crushed bamboo is greater than that of chips, and the lightest species float for only ten minutes while the heavier sink at once. Chips will float for  $2\frac{1}{2}$  hours (see paragraph 7).

14. I therefore come to the conclusion that the chief difficulties hitherto found in the digestion of bamboos are of a physical rather than a chemical nature and they must be, and can be, conquered by physical means. To recapitulate, they are, or have been:—

- a. The impossibility of digesting nodes.
- b. The tendency to float.
- c. Mass resistance to liquor penetration considerably greater than that of spruce and varying with the size of the chip.



- d. Capillary air resistance to liquor penetration.
- e. Resistance increasing with age.
- f. A possible colloidal resistance of gelatinised pectose.

Each and all of which are wholly got rid of or very much reduced in difficulty by crushing.

15. One of the difficulties remaining is connected with the starch content of the plant and its effect upon yield of cellulose and also on the bleaching results. In its annual reproduction of new culms, bamboo is unique, inasmuch as the whole of these reach their full height within a period of from two to four months. This enormous and rapid effort may result in new growth equalling, in actual dry weight, one-fifth to one-fourth of that of the whole clump, and the normal activity of its root and leaf systems would be wholly inadequate to support it were these not aided by its power of storing up large reserves of plant food in anticipation, chiefly in its roots but also to a very considerable extent in its culms. From these reserves the young shoots draw the major portion of the material required for building up their tissues. These reserves consist of starch in its solid and granular form. During the process of its transformation into woody tissue it breaks down, or metamorphoses, into several groups of secondary products, all of which are soluble in cold water and therefore capable of being assimilated by the plant. Both as starch and as secondary starchy matter, it at all times and seasons forms a considerable constituent of bamboo and one not met with to any appreciable amount in other raw materials. But its special interest to us is its liability to large variation at different seasons of the year. As the young culms make their appearance at about three to five weeks after the commencement of the southwest monsoon, we find the largest reserve stores existing then, the first few weeks of the monsoon season, as also the period of showery weather preceding it, having been utilised to collect them; and we also find, as we should expect, that they are at their lowest at six to eight weeks after the monsoon has ceased and when the young stems are fully grown. But should a period of showery weather intervene during seasons which are usually dry, or if the district is visited by the short northeast monsoon, the habit of the plant asserts itself and storage takes place, resulting in the upsetting of

the normal relative percentage of its constituents. I have found, for instance, in a bamboo cut during the height of the dry season a total water extract of 9 per cent on the dry substance, a period of unusual and unseasonable showery weather, lasting for three weeks, then intervened. A culm cut from the same clump then yielded 23% of water solubles with, of course, a relative reduction of the cellulose which was only 37%. But it is important to note that this same culm, preserved in a dry atmosphere for five weeks, yielded then only 15 per cent of water extract, which three months later fell to 11 per cent with corresponding rises in the relative percentage of cellulose. This can only mean that the starch is, in its secondary forms, capable of being oxidised by air and dispersed in the atmosphere, and that such oxidation is an integral part of the process of seasoning, and it forces us to the conclusion that the maximum relative yield of cellulose can only be obtained from bamboo which is not merely dry but is also *seasoned*. We have in this a highly probable reason for the few instances of 33% to 35% yields reported. In my own experiments, numbering some hundreds, results obtained from *seasoned* bamboo of all five species run to a remarkably close and regular average of 45% of unbleached pulp.

16. The influence of the starch content upon bleaching is due to the result of the combination between it and NaOH which occurs under the digestion conditions of strong liquor and high temperature. A detailed analysis of the water solubles of a stem cut at a period when the food stores were being used gave the following results:

|                                    | Per cent |
|------------------------------------|----------|
| Starch, solid                      | 2.70     |
| Starch in secondary forms          | 8.33     |
| Colouring matter and soluble salts | 2.54     |
|                                    | <hr/>    |
|                                    | 13.57    |

The result of the combination of solid starch with NaOH is colourless and soluble and so does no harm, but that with the secondary starch matter is an insoluble dark brown precipitate which the pulp filters out and which is unbleachable (within

economic limits) and seriously affects the bleaching of the pulp. The quantity of NaOH which may thus be abstracted from the liquor is about 0.22 for each 1% of solubles present, so that with a sample containing 9%, about 2% of NaOH, on weight of raw material, will be thus used up. Since they are soluble in hot water, obviously the right course is to make a preliminary boiling in water the first step in digestion. After thus exhausting them the digestion can then proceed with a reduced quantity of NaOH. Pulp thus treated will bleach with 4 to 6% less bleaching powder.

17. Notwithstanding the improved bleaching conditions thus brought about, the bleaching qualities of the pulp, when prepared with the *minimum* quantity of NaOH required for digestion, still leave much to be desired. A typical result, on crushed and starch-exhausted *Bambusa polymorpha*, is as follows:

|  |             |
|--|-------------|
| NaOH, on air dry weight of raw material                    | 16%         |
| Initial temperature for 1 hour                             | 177 deg. C. |
| Subsequent temperature for 4 hours                         | 162 deg. C. |
| Duration of digestion                                      | 5 hours     |
| Unbleached yield, air dry                                  | 50%         |
| Bleaching powder used on A.D. weight of<br>unbleached pulp | 36%         |
| Bleached yield, air dry                                    | 44.5%       |

The digestion was perfect as far as freedom from chips and imperfectly digested material goes but the pulp was of a very dark brown colour and required 36% of bleaching powder to bring it up to a brilliant white. The wide difference between the unbleached and bleached yields will be noted and is clearly due, in large measure, to precipitation of colouring matter which can only come from the gelatinised pectose which, as already remarked, is dark brown in colour, and is almost unbleachable. A problem familiar to all paper-makers who pulp grasses is the extent to which it is profitable to gain in colour at the expense of yield by using an excess of NaOH. Such excess does intensify hydrolysis of fibre but with the compensation of improved colour, presumably either by holding the coloured products more perfectly in solution, thus permitting them to be more thoroughly washed out of the

pulp, or by changing them to compounds of lighter colour. A series of experiments to determine the profitable limit of excess for bamboo resulted in it being fixed at 4%. The average result with exactly similar conditions of material, temperature and duration of digestion as quoted above being:

|                       |       |
|-----------------------|-------|
| NaOH                  | 19½%  |
| Unbleached yield      | 45.5% |
| Bleaching powder used | 25%   |
| Bleached yield        | 43%   |

That is to say, an excess consumption of 3½% of NaOH resulted in a loss of 1½% in the final result and saving of 11% of bleach. This was satisfactory but not wholly so and we therefore endeavoured to find a better solution of the difficulty in the sulphate modification of the soda process. This process seemed to be very clearly indicated when we found that a one per cent solution of sodium sulphide, applied in simple cold steeping to the unbleached pulp produced by NaOH, dissolved out of it a large quantity of dark brown colouring matter, leaving it several shades lighter in colour and much more bleachable.

18. The liquor used contained sodium sulphide and hydroxide in the proportion of 1:3. In the following average result the whole is reckoned in terms of NaOH. Material, temperature and duration of digestion as before.

|                       |      |
|-----------------------|------|
| NaOH                  | 20½% |
| Unbleached yield      | 46%  |
| Bleaching powder used | 17%  |
| Bleached yield        | 44%  |

The soda required is 1% more than with straight soda liquor as a compensatory allowance for the lower digestion efficiency of the Na<sub>2</sub>S, but the bleaching effect of the latter, as also its influence in retarding hydrolysis of fibre, is most marked and undeniable, and our final conclusion is that the objections which have been made to bamboo as a paper-making material and the difficulties hitherto met with in its treatment, *viz.*, irregular yields,

floating, resistance to bleaching, mass, capillary air and colloidal resistance to liquor penetration causing irregular and imperfect digestion, the difficulty of dealing with mixed ages and the impossibility of economically treating the nodes, — can all be met and solved and the whole problem reduced to one of extreme simplicity by the adoption of a scheme of treatment embracing the following features:

- I. Seasoned bamboo only to be used.
- II. Raw material to be crushed.
- III. Water solubles to be extracted previous to digestion.
- IV. Digestion with sulphate liquor.

19. It should be understood that the foregoing refers only to the five leading species of India and Burma and may not prove altogether applicable to bamboos of other species grown elsewhere.



## A NEW TECHNICAL DETERMINATION OF BLEACHING QUALITY OF SULPHITE PULP

BY DR. ERICH RICHTER

*Hawkesbury, Ont.*

In May, 1912,<sup>1</sup> I had been able to show that what is called the Hempel's nitric acid figure of pulp, that is, a treatment of sulphite or other pulp with a 13 per cent nitric acid for one hour in a boiling water bath, drawing air through and measuring the gases produced, can be easily converted in a method to determine the percentage non-cellulose in pulp, jute, or wood.

To get Hempel's nitric acid figure,<sup>2</sup> ordinary pulp, for instance, is somewhat broken up and submitted to a treatment with nitric acid as mentioned above. The gases are drawn through suitable absorption apparatus filled with water and at last with sulphuric acid. The nitric and nitrous acids which are formed can be titrated with standard solution of permanganate of potassium and one hundred normal caustic soda solution.

In order to get the percentage of non-cellulose or lignin, the same operation is done with pulp, which has been previously extracted with ether, alcohol and water. The percentage of lignin is then figured with a proper standard figure for jute or wood. For spruce wood I have found 1,076 grs.  $\text{N}_2\text{O}_3 = 28\%$  lignin and for the nitric acid figure 0,8048 I made equal 40.

Investigation of both kinds on quite a number of different sulphite pulps, together with other tests, showed that the nitric acid figure gave values proportional to the bleach test, and as the latter is not very convenient, for instance, when it is necessary to test one, two, or more carloads of pulp on bleaching quality in a few hours, as it often happens in a pulp or paper mill, it has been tried to replace the same by the nitric acid figure. Being unable to find the right formula to convert this figure in per cent bleach powder for the pulp sample in an endeavor to reduce the time used for testing and to make the method as simple as possible,

<sup>1</sup>Wochenblatt für Papierfabrikation p. 1631.

<sup>2</sup>Hempel v. Seidel,  $\frac{1}{2}$  Diss. Dresden.

it occurred to me that a color test might do the work, provided it would give results within half per cent.

According to Klason,<sup>1</sup> the non-cellulose in pulp can be tested colorimetrically when ordinary pulp is treated with standard sulphuric acid. In Germany, a mixture of 4 parts of concentrated acid and 1 part of water is used. Others use stronger acids.

With sulphite pulps of different origin, tested on lignin, cellulose, bleaching quality, etc., series of experiments were made according to Klason, using one or another pulp as a standard sample. Unfortunately, in too many cases the results differed so much, not only in comparison with different percentage on non-cellulose, but also compared with the bleaching quality, that it was obvious that this method could not replace either the lignin test or the test for bleaching. It could be easily seen that sulphite with little non-cellulose, but soft-cooked, gave a much darker color with sulphuric acid than a strong-cooked pulp which sometimes contained 2% more lignin, that is, about equivalent to 7-8% more bleach powder. The reason for this is that a sulphuric acid not only attacks the non-cellulose, but also, especially in the case of soft pulp, it attacks too much the pure cellulose. After trying the method with sulphuric acid of different strengths and failing to get good results, another acid was used. Naturally, attention was drawn towards the diluted nitric acid.

Preliminary tests with nitric acid (about 13%  $\text{HNO}_3$ ) showed sufficient agreement, and further investigations proved the success of this method, tests with it sometimes causing the revision of ordinary experiments on bleaching quality.

To make a test 5 grs. of air-dried pulp are broken up in thin pieces, put in a wide-necked bottle together with 100 cc. of standard nitric acid, well shaken, and kept for about one hour in a dark place. After that time it is again well shaken and the pulp filtered off, best by means of a little piece of pure absorbent cotton in the bottom of a dry funnel. From the liquid 25 cc. are taken and poured in a small bottle. With standard pulp of well known bleaching quality the same operation is performed at the same time, and both liquids are now compared in color. From a burette water is added to the darker one until the shade of both solutions

<sup>1</sup>Papierzeitung 35, 3781.

is the same. Suitable amounts of each acid solution are then put in Eggertz carbon tubes and compared. This is best done by looking down from the upper end, keeping a white paper below and using different amounts, once 5 cc., another time 10 cc. Should the colors not be uniform, as an additional check, a greater depth of the lighter liquid is used until the shades are the same. It is then easy to figure the bleaching capacity of the unknown sulphite.

| %Bleach powder                       | Total amount of acid<br>a. water used |
|--------------------------------------|---------------------------------------|
| Standard pulp . . . 8,5%             | 25 cc.                                |
| Unknown Sulphite . . . x             | 25 cc. $\times$ 12 cc.                |
| $x = \frac{8,5 \cdot 37}{25} = 12,6$ |                                       |

Should the first test be spoiled, another 25 cc. can be used without delay.

When breaking up the pulp, not much time is spent, as it need not be finely beaten up like in a regular bleaching test. A moisture test of the pulp should be made, at the same time, although it is not necessary to be very exact, as I have found that a few per cent difference in moisture does not influence the result to any noticeable extent, owing to the great excess of intric acid. When wet pulp has to be tested it must be dried somewhat and in order to facilitate the operations it is best broken up first. One thing more should be mentioned; a very strong cooked pulp sometimes would not color the acid after only one hour. In case a test cannot be delayed, the bottles are placed in a water bath of about 40° C. and frequently shaken. The temperature should not exceed 45°C. In about 15 minutes the acid colors almost instantaneously, and after cooling down a little the test is made as described above.

Performed in one way or the other, the method gave excellent results, compared with the regular test for bleaching quality, in all cases far more exact than is necessary at any time for technical purposes. If largely varying grades of pulps are to be determined, it is well, of course, to use correspondingly different standard pulps; for instance, one with 8, 12 and 16% bleach quality, although it is not absolutely necessary. I have been using many

times pulp with 6% capacity of bleaching as normal and have tested with it other samples which needed 14% bleach powder or more.

At last I might state that it may be possible to find some standard color solutions for different percentages, thus reducing again the time used for testing, although so far, experiments in this line have not been successful. In the following table, some bleach tests are given and combined with a few of them, Hempel's nitric acid figure, the percentage of lignin, cellulose, etc.

| Pulp Sample No. | % Bleach powder New Method | % Bleach powder Old Method | Hempel's Nitric Acid Figure | % Ether Pitch | % Alcohol Pitch | % Water Extract | % Ash | % Lignin | % Cellulose |
|-----------------|----------------------------|----------------------------|-----------------------------|---------------|-----------------|-----------------|-------|----------|-------------|
| 1               | 5,6                        | 5,5                        | 5,8                         | 1,14          | 0,13            | 0,13            | 0,29  | 2,7      | 95,5        |
| 2               | 8,3                        | 8,4                        | 7,7                         | 1,17          | 0,19            | 0,15            | 0,36  | 3,2      | 95,0        |
| 3               | 6,9                        | 6,9                        | 6,4                         | 1,09          | 0,45            | 0,11            | 0,28  | 2,9      | 95,1        |
| 4               | 15,6                       | 15,6                       | 15,9                        | 1,05          | 0,26            | 0,52            | 0,46  | 5,6      | 91,9        |
| 5               | 14,5                       | 14,8                       | 7,2                         | 0,65          | 0,21            | 0,71            | 2,07  | 4,9      | 91,4        |
| 6               | 7,9                        | 7,8                        |                             | 1,11          | 0,09            | 0,23            |       |          |             |
| 7               | 7,3                        | 7,3                        |                             | 1,03          | 0,12            | 0,27            |       |          |             |
| 8               | 5,7                        | 5,6                        |                             | 1,10          | 0,26            | 0,12            | 0,22  |          |             |
| 9               | 6,1                        | 6,2                        |                             | 1,06          | 0,17            | 0,11            | 0,28  |          |             |
| 10              | 11,4                       | 11,2                       |                             |               |                 |                 |       |          |             |
| 11              | 13,8                       | 14,1                       |                             |               |                 |                 |       |          |             |
| 12              | 5,4                        | 5,4                        |                             |               |                 |                 |       |          |             |

These figures show in regard to the new and old bleach tests sufficient accordance to make the former one a suitable method for testing pulp in a short and simple way, and if it would be used only to prevent the enormous waste of manufacturing newspaper from high-grade pulp, it is serving one of its purposes.



## NOTES ON COMMERCIAL DEXTRINS

BY G. W. ROLFE

While the term "dextrin" is often used to designate a class of compounds of more or less definite composition formed by the transformation of starch whether hydrolytic or otherwise, the commercial products known as "dextrins" are almost invariably made by roasting starch, which in many cases has been previously moistened with dilute acid, the heat being usually between 140° and 200° C. according to the qualities desired in the product. Only a few special "gums" which are classed as dextrins are products of a mild acid hydrolysis of water suspensions of starch after the manner of glucose manufacture.

From time to time covering a period of some years, I have carried on an investigation of these "torrefaction" dextrins with the object of learning more of their composition, particularly with reference to their relation to the products of acid hydrolysis.

In this work I have been assisted by my students, notably by the late George F. Ulmer and William White. The investigation has been frequently interrupted and is far from complete, but it seems appropriate to publish some of the work at this time.

Thirteen samples of commercial dextrins, supplied to us by a prominent manufacturer as typical products, were examined as to their behavior with iodine, optical rotation and cupric reducing power. No information was furnished as to the details of manufacture of these samples. In general, it is understood that "dextrins" are made by moistening the practically dry starch with dilute acid, preferably nitric, and roasting the mass at comparatively low temperatures, while the "British gums" are not treated with acid but roasted at a higher temperature. In the preparation of many of these dextrins, different characteristics are given by blending the more or less completely roasted products in varying proportions. Products of this latter class are usually more or less dark colored from the effect of the high temperature.

It is somewhat difficult to obtain solutions of many of these dextrins which are clear enough for polarizing. The treatment



which has seemed to work best is to bring the solutions to a boil, filter while hot and then rapidly cool the filtrate with running water.

The following table gives the results of the investigation of these thirteen dextrans:

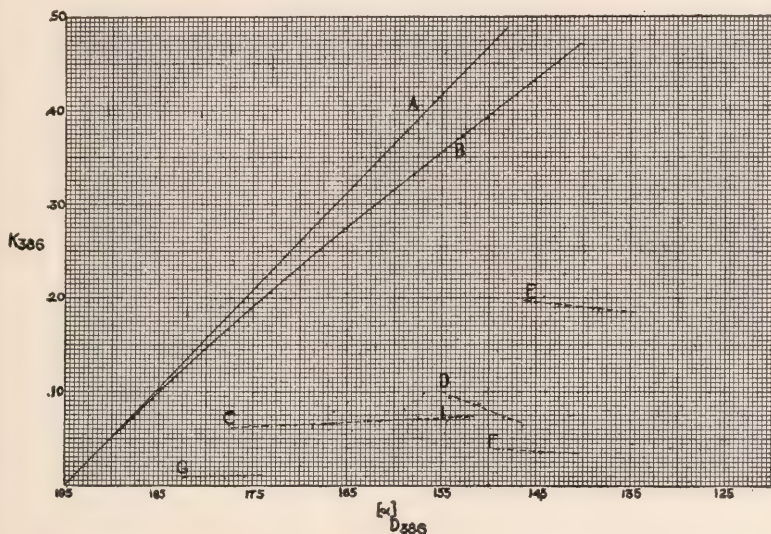
TABLE I  
ANALYTICAL DATA OF COMMERCIAL DEXTRANS

| Name                                 | I test    | $[\alpha]_{D386}^{20}$ | $K_{386}$<br>(Dextrose—1.00) |
|--------------------------------------|-----------|------------------------|------------------------------|
| 1. German Std. Canary                | Red       | 161.2                  | .0886                        |
| 2. Superior Dextrin                  | Violet    | 174.0                  | .0342                        |
| 3. German Std. White<br>Potato       | Wine red  | 176.6                  | .0778                        |
| 4. German Std. Light<br>Canary       | Red Brown | 156.5                  | .0673                        |
| 5. White Potato                      | Wine red  | 181.8                  | .0832                        |
| 6. German Dextrin                    | Red       | 169.4                  | .1508                        |
| 7. Potato Canary                     |           | 156.6                  | .0778                        |
| 8. Tapioca<br>Envelope No. 1         | Brown     | 174.0                  | .0374                        |
| 9. Envelope No. 2                    |           | 166.2                  | .0562                        |
| 10. Corn Dextrin                     | Brown     | 149.8                  | .0802                        |
| 11. German Std.<br>White Potato      |           | 177.1                  | .0840                        |
| 12. Imported English<br>Envelope     | Brown Red | 180.6                  | .0420                        |
| 13. Imported German<br>Potato Canary |           | 154.3                  | .0733                        |

It will be seen at once that these bodies, while showing iodine reactions and optical rotations like acid-hydrolysed starch products, have a very low copper reduction value. The plotted relations between specific rotation and copper reduction show no well-defined curve. As many of these commercial dextrans were probably mixed products, we next made dextrans in the laboratory under known conditions, applying as far as possible the fundamental principles of manufacture employed commercially.

Ten grams of potato starch were moistened with 3 cc. of dilute nitric acid (1 part of 1.44 acid in 100 cc. of water) and intimately mixed by rubbing with a pestle so as to obtain a homogeneous

# RELATION OF SPECIFIC ROTATION TO CUPRIC REDUCTION OF TORREFACTION DEXTRINS



mass. The mixture was then spread out over the bottom of a flat porcelain dish and heated in an oven kept at 110–115°. Iodine tests were made on solutions of the dextrin produced.

The following are the results obtained:

Temp. = 115°

| Time of Heating<br>Minutes | Color with<br>Iodine |
|----------------------------|----------------------|
| 0                          | Blue                 |
| 15                         | Blue                 |
| 30                         | Blue                 |
| 45                         | Violet-blue          |
| 60                         | Violet               |
| 75                         | Red-violet           |
| 90                         | Rose-red             |
| 105                        | Red                  |
| 120                        | Red-brown            |
| 135                        | Red-brown            |
| 240                        | Red-brown            |
| 300                        | Red-brown            |

TABLE II

OPTICAL AND REDUCING CONSTANTS OF DEXTRINE MADE IN  
LABORATORY*Series I*

| (3 cc. of $\text{HNO}_3$ ) | Temperature = 110–115°C.) |                  |
|----------------------------|---------------------------|------------------|
| Total Time of Heating      | Specific Rotation         | Cupric Reduction |
| (hours)                    | $[\alpha]_{D386}^{25}$    | $K_{386}$        |
| $3\frac{3}{4}$             | 168.7                     | .0614            |
| $2\frac{1}{2}$             | 168.0                     | .0645            |
| 5                          | 163.2                     | .0682            |
| $2\frac{3}{4}$             | 172.4                     | .0636            |
| 2                          | 175.0                     | .0682            |
| 3                          | 172.0                     | .0595            |
| 6                          | 173.3                     | .0629            |
| $4\frac{3}{4}$             | 176.0                     | .0575            |
| $5\frac{3}{4}$             | 175.3                     | .0639            |
| 5                          | 164.4                     | .0579            |
| 10                         | 158.9                     | .0802            |
| 6                          | 166.3                     | .0796            |
| 9                          | 161.8                     | .0843            |
| 10                         | 162.5                     | .0731            |
| 14                         | 153.5                     | .0702            |
| $8\frac{1}{2}$             | 157.9                     | .0501            |
| 14                         | 154.4                     | .0696            |
| 16                         | 158.6                     | .0573            |
| 23                         | 156.9                     | .0979            |

*Series II*(Heated with 6 cc.  $\text{HNO}_3$ )

|                |       |       |
|----------------|-------|-------|
| 5              | 151.1 | .0862 |
| 13             | 148.4 | .0730 |
| $6\frac{1}{2}$ | 154.1 | .0946 |

*Series III*(Reheated  $1\frac{1}{2}$  hours with 3 cc. more  $\text{HNO}_3$  added)

|                 |       |      |
|-----------------|-------|------|
| $10\frac{1}{2}$ | 136.5 | .186 |
| $12\frac{1}{2}$ | 141.5 | .185 |
| 15              | 136.3 | .262 |
| 12              | 144.2 | .201 |

*Series IV*(Reheated  $1\frac{1}{2}$  hours at  $165^{\circ}$  after previous heating with 3 cc.  $\text{HNO}_3$ )

| Time<br>Hours | Specific Rotation | Supric Reduction |
|---------------|-------------------|------------------|
| 9             | 148.4             | .0385            |
| 6             | 147.0             | .0369            |
| 20            | 142.4             | .0351            |

*Series V*

(Heated without acid)

|                |       |       |
|----------------|-------|-------|
| 5              | 181.4 | .0092 |
| 6              | 177.8 | .0074 |
| 10             | 175.8 | .0096 |
| 8              | 179.5 | .0118 |
| $7\frac{1}{2}$ | 179.1 | .0123 |

These are the characteristic iodine colors shown by the transformations of starch and in the regular sequence of color change which marks the progress of acid hydrolysis.

The following investigations were then carried out: (1) A number of samples of potato starch were made up with nitric acid as described and heated for varying lengths of time at  $110$ – $115^{\circ}$ . (2) Similar heat treatments were given starch mixed with double the amount of acid. (3) After heating for some time, samples made up as in (1) were treated with more acid and again heated. (4) Starch treated as in (1) was again heated at a higher temperature ( $165$ – $170^{\circ}$ ) in an aniline bath. (5) Starch without acid treatment was heated to  $165$ – $170^{\circ}$ . An investigation similar to that applied to the commercial samples of dextrins was made on these laboratory products and the results are tabulated below. (Table II). Plots of the relation of the specific rotation of these dextrins to their cupric reduction are also given.

Referring to this plot: Line A represents the relation between the specific rotation and cupric reduction of normal diastase-hydrolysed starch products; line B showing the same relation for normal acid-hydrolysed starch products. Lines C, D, E, F, and G show the corresponding relations of specific rotation to cupric reduction of the laboratory dextrins of Groups 1 to 5, respectively, and which are described above.

All these plotted values show that while the specific rotatory values decrease with continued heating, the cupric reduction remains practically constant. A study of these plots lead us first to the conclusion that probably a normal hydrolytic action begins on the starch, but very soon ceases owing to the evaporation of the hydrolytic agent, although a molecular change tending to a simplification of structure, as evidenced by the gradual diminishing of the specific rotation during the roasting as well as the corresponding iodine reactions proceeds continuously. That the slight cupric reducing power might be caused by normal acid hydrolysis seemed to be shown by the fact that in the Line G which represents products made by heating alone, after the manner of making the "British gums," the reducing powers are extremely slight as might be expected from the assumption that any hydrolysis proceeds simply from the action of moisture and weak acids originally present in the starch or produced by the heating. Starch treated with a larger proportion of acid, as shown in Line D, shows more reduction, as would be expected, although these results are not so pronounced as would be expected. This is partially accounted for in these samples by the fact that the volume of the acid solution was somewhat too large so that the starch was pasted slightly, preventing normal heat conditions throughout the mass. Line E shows the effect of adding more acid and reheating at 110–115° and indicates considerable hydrolysis. Line F showing products retreated with acid and reheated but at a higher temperature, shows a lower rotation but also a lower reduction. This is readily explained, however, as the product was highly colored, showing decomposition by the heating which would affect rotation and reduction alike.

An investigation was then carried out to learn more definitely whether the reduction value was actually caused by hydrolysis, and, further, what influence a more complete purification of the starch had upon the production of the reducing power in gums made by roasting starch without added acid.

As pure a starch as possible was made by treating a good quality of commercial potato starch with a 0.5% solution of potassium hydrate, keeping the granules in suspension by means of an air-blast. This treatment was continued for an hour, the starch then



allowed to settle and washed several times by decantation. The starch was then subjected to a similar treatment with a 1% hydrochloric acid solution, washing as before and then dried over sulphuric acid in a vacuum, 10 hours at 50°C. and then 20 hours at 100°. A test on the ash of the purified starch gave: 0.066%. Corn starch purified in the same way had 0.035% ash. The unpurified starches had, for potato, 0.21% ash, corn, 0.15%.

A preliminary roasting of two samples of the original potato starch and two of the purified, the samples being heated in copper vessels in an oil-bath at 156°C. and tested hourly, gave the following results.

Nos. 1 and 2 are the original starch, 1 being heated in an open crucible; 2 in a closed one; 3 and 4 being the same starch purified and heated in an open and a closed crucible, respectively.

## IODINE TESTS

| Time of heating | No. 1       | No. 2       | No. 3       | No. 4       |
|-----------------|-------------|-------------|-------------|-------------|
| 1 hour          | Blue        | Blue        | Blue        | Blue        |
| 2 hours         | Blue        | Blue        | Blue        | Blue        |
| 3 hours         | Blue        | Blue        | Blue        | Blue        |
| 4 hours         | Blue        | Blue-violet | Blue-violet | Blue-violet |
| 5 hours         | Blue        | Blue-violet | Blue-violet | Blue-violet |
| 6 hours         | Blue        | Blue-violet | Blue-violet | Blue-violet |
| 7 hours         | Blue        | Blue-violet | Blue-violet | Violet      |
| 8 hours         | Blue        | Violet      | Violet      | Violet      |
| 9 hours         | Blue-violet | Violet      | Violet      | Red-violet  |
| 10 hours        | Blue-violet | Violet      | Red-violet  | Red-violet  |
| 11 hours        | Violet      | Violet      | Red-violet  | Deep red    |
| 12 hours        | Red-violet  | Violet      | Red-violet  | Deep red    |

These iodine tests, which were made on samples which had been boiled up with water and cooled, show the characteristic

changes in color of preliminary hydrolysis, the purified and anhydrous starch apparently showing more change than the commercial material which had about 10% or more of moisture. This is also shown in the following table of specific rotations and cupric reducing powers of the aqueous solutions of some of these samples:

| (After 8 hours' heating)  |                     |                                |
|---------------------------|---------------------|--------------------------------|
| Number                    | $[\alpha]_{D386}^b$ | $K_{386}$<br>(Dextrose = 1.00) |
| 1                         | 178.1               | .015                           |
| 2                         | 176.5               | .0117                          |
| 3                         | 172.9               | .0002                          |
| 4                         | 169.1               | .0169                          |
| (After 12 hours' heating) |                     |                                |
| 1                         | 174.5               | .0246                          |
| 2                         | 174.8               | .0219                          |
| 3                         | 171.6               | .0163                          |
| 4                         | 162.1               | .0314                          |

Another series of heat transformations were carried out by the more effective arrangement of heating the starch spread in thin layers in flat dishes placed on shelves in a jacketed hot-air oven, kept at 165–170°C. by a thermostat.

These latter experiments were carried out with the intention of throwing some light on the effect of moisture on the formation of reducing substance.

Purified and commercial corn and potato starches were heated for different lengths of time and allowed to cool between successive heatings to absorb moisture from the air. Two batches of the commercial corn starch were then heated under similar conditions and one set cooled by being exposed to the air, the other in a vacuum dessicator between successive heatings.

The results are given in the following table:

| Starch Sample                 | Time of<br>total<br>heating | Specific Rotation<br>[ $\alpha$ ] <sup>D</sup> <sub>386</sub> | Cupric Reduc-<br>tion <sup>K</sup> <sub>386</sub> |
|-------------------------------|-----------------------------|---|---|
| Purified corn                 | 4 hours                     | 160.2   | .0148   |
|                               | 6 hours                     | 157.8   | .0234   |
|                               | 8 hours                     | 129.8   | .0197   |
| Com. Potato                   | 4 hours                     | 187.8   | .0171   |
|                               | 6 hours                     | 185.2   | .0119   |
|                               | 8 hours                     | 184.0   | .0119   |
|                               | 11 hours                    | 154.8   | .0208   |
| Purified Potato               | 4 hours                     | 175.0   | .0116   |
|                               | 6 hours                     | 178.1   | .0176   |
|                               | 8 hours                     | 164.2   | .0214   |
|                               | 11 hours                    | 159.5   | .0213   |
| Com. corn exposed<br>to air   | 2 hours                     | 182.9   | .0079   |
|                               | 3 hours                     | 180.5   | .0087   |
|                               | 5 hours                     | 179.9   | .0115   |
| Com. corn cooled in<br>vacuum | 3 hours                     | 185.9   | .0118   |
|                               | 5 hours                     | 178.4   | .0111   |
|                               | 6 hours                     | 173.1   | .0176   |

It is perhaps premature to formulate conclusions from the data at hand. What has been established is that dry heat produces a cleavage of the starch molecule on lines similar to that caused by hydrolysis. Substances are formed which have a cupric reducing power of .01-.02 (dextrose=1.00) but apparently they are not the result of any hydrolytic action of the moisture or acid bodies in the original starch, (see recent work of Malfitano and Moschkoff, *Compt. rend.*, 154,443, in this connection) but may be due to a dextrose radical in the starch molecule which is included in the "stable" dextrin complex, as indicated in the work of Brown and Millar. (*Jour. Chem. Soc.*, 75, 315).

It follows that those commercial dextrans showing reducing power more than .02 have been made by an acid treatment, the amount of acid used being indicated by the increase in reduction over .02, the time and degree of the heating being indicated by the specific rotation.



## UBER HALBZELLSTOFFE

VON CARL G. SCHWALBE

*Eberswalde b. Berlin, Germany*

Als Hauptbestandteile der Hölzer nimmt man Zellstoff-Lignin und Kohlehydrate an. Es muss beidem derzeitigen Stande der Forschung dahingestellt bleiben, ob die se Körper gruppen miteinander in chemischer Bindung sind oder nur ein Gemenge darstellen, ebenso was Lignin eigentlich ist. Unsere Aufschliessprocesse entfernen zum grössten Teil das Lignin und die Kohlehydrate also die "Nichtcellulose." Als Halbzellstoffe will ich nun alle diejenigen Zellstoffarten bezeichnen, die in ihrem Cellulose-bezw. Ligningehalt zwischen reinen Zellstoffen einerseits und Holz andererseits stehen. Je nach den angewendeten Verfahren ist diese Aufschliessung mehr oder weniger weitgehend. Wird mit heissem Wasser aufgeschlossen, wie es bis zu gewissem Grade beim Heisschliff geschieht, so steht das entstehende Produkt in seiner chemischen Zusammensetzung dem Holze noch ausserordentlich nahe. Voraussichtlich sind es kleine Mengen von Kohlehydraten die herausgelöst werden: denn *Klason* hat gezeigt, dass man durch heisses Wasser solche Kohlehydrate aus feinzertheiltem Holz herauslösen kann. Beim Braunholzschliff ist durch den Dampfprocess die Aufschliessung schon weiter gegangen, etwa 10-20% des Holzmaterials sind verschwunden. Der Cellulosegehalt des Braunschliffs weicht jedoch nach *Zacharias* von dem des Holzes kaum ab; man muss daher annehmen dass durch den Dampfprocess der Zellstoff des Holzes so verändert wurde, dass er zum Teil der Wirkung des Chlors bei der von *Zacharias* verwendeten Cellulosebestimmungsmethode von *Cross* und *Bevan* nicht mehr zu widerstehen vermag. Scheinbar hat also die Menge der Inkrusten eine Änderung nicht erfahren, wohl aber ist eine Veränderung der Art der Inkrusten nachweisbar. Braunholz liefert bei der Prüfung auf Phloroglucinadsorptionsvermögen andere Werte als Holz den Zellstoffen ausserst nahestehend in Bezug auf Cellulose—besser auf Ligningehalt sind die Kraftzellstoffe. Auch hier zeigt sich wieder die Unmöglichkeit



mit der *Cross* und *Bevan*'schen Chlorierungsmethode Unterschiede im Zellstoffgehalt zwischen normalen Natronzellstoffen und Kraftzellstoffen aufzufinden. Auch heir mag die Ursache in mangelnder Widerstandsfähigkeit der durch den scharfen Kochprocess geschädigten Natronzellstoffe liegen. Sie werden vielleicht vom Chlor stärker angegriffen als die Kraftzellstoffe. Ebenso wahrscheinlich aber ist es, dass nicht vorzugsweise die Menge der Inkrusten, sondern die Art der Inkrusten die Unterschiede bedingt. Da sich auch im Ligningehalt (bestimmt durch die Phloroglucinadsorption keine Unterschiede zeigen, sind es wohl die Kohlehydratreste, welchen die verschiedene Festigkeit der Kraft—und Natronzellstoffe zuzuschreiben ist. Die *Klason*'sche Ligninprobe, die Hydrolyse u. am. lassen gewisse Unterschiede der genannten Zellstoffarten erkennen Theoretisch sind zwischen den Extremen: Holz und Zellstoff zahllose weitere Übergangsstufen denkbar. Gelingt es weitere solche Zwischenstufen festzuhalten, so sind wissenschaftliche und technische Erfolge zu erwarten. Wissenschaftliche Erfolge, weil das Studium der Halbzellstoffarten die bei Auflösung der die Faserbündel verkittenden Substanzen entstehen, Aufschlüsse über die Natur der Kittsubstanzen bringen kann. Ein allmählich fortschreitender stufenweise gesteigerter Aufschluss wird am besten geeignet sein die Natur des Holzes zu entratseln. Ich habe solche Studien begonnen. Das bisherige wissenschaftliche Ergebnis ist, das die *verkittenden* Stoffe die Träger der Farbreaktionen auf Lignin sind. Diese Reaktionen verschwinden schon wenn noch 80–90% des Holzmaterials vorhanden sind. Die farbgebenden Stoffe treten demnach nur in relativ untergeordneter Menge auf; sie machen *nicht* die Hauptmenge des sogenannten Lignins aus. Aus dem weiteren Abbau solcher Halbzellstoffe erhoffe ich allmahliche Entratselung des Lignins Technische Erfolge sind erzielt, wenn es gelingt den Faserverband des Holzes soweit zu lockern, das sich die Faserbündel durch Kollergangarbeit unter Verlust von nur 10–20% seiner Menge in einen Brei aus verholzten Fasern verwandeln lassen, der außerordentlich zähe feste Papiere ergibt, die je nach den Einzelheiten des angewendeten Aufschliessverfahrens saugend oder völlig leimfest sind. Diese Papiere können in der Farbe des weissen Holzschliffes und dunkler Natronzellstoffe hergestellt

werden. Sie vergilben nicht oder nur sehr wenig. Sie werden daher in den meisten Fällen reine Zellstoffpapiere ersetzen können und bei Papieren aus Zellstoff und Holzschliff bedeutet der Ersatz des Zellstoffs durch ein Surrogat weitere Verbilligung. Denn bei der Herstellung des Zellstoffs sind über 50% des Materials verloren gegangen: bei der Herstellung des Surrogates nur 10–20%. Weitere Vorteile ergeben sich, weil der Aufschliessprocess, eine Modification des Sulfitkochprocesses, dem sich die bestehenden Kochersysteme unschwer anpassen lassen schon in 3–6 Stunden durchgeführt werden kann. Es läßt sich demnach die Apparatur weit stärker ausnutzen; auch ist der Warmeverbrauch weit geringer. Die neuen Halbzellstoffe ergeben nach der *Cross'* schen Chlorierungsmethode viel zu hohe Zellstoffzahlen für Lignin nach der Absorptionsmethode aber ebenfalls. Diese Methoden lassen sich also in ihrer gegenwärtigen Form nicht auf die neuen Halbzellstoffe anwenden. Wie schon erwähnt, reagieren sie mit dem Phloroglucin-oder Salzsaurereagens nicht oder wesentlich schwächer als Holz.

Das angewendete Verfahren gestattet auch Halbzellstoffe herzustellen, die sich in ihrem Cellulosegehalt den üblichen Sulfitzellstoffen annähern, man braucht nur die Aufschliessdauer entsprechend zu verlängern, bezw. die Concentration der aufschliessenden Flüssigkeit (einer Sulfitdauge) zu erhöhen. Es bietet sich aber auch die Möglichkeit: anstelle des Aufschlusses durch weitere längere Druckerhitzung, die von schädigendem Einfluss auf die Festigkeit der Faser sein kann, die Aufschliessung ohne Druck zu setzen. Schon *Kellner* hat versucht Holz mit electrolysierten Kochsalzlaugen mit aber auch ohne Druck aufzuschliessen. Der Electrolyse im Druckgefäß vermochte die Apparatur nicht zu widerstehen: die Electrolyse ohne Druck verlangte feine Verteilung des Holzes. Der erwähnte Halbzellstoff läßt sich nun da er als Faserbrei vorliegt, weit leichter aufschließen als harte Holzstücke. Es besteht also die Möglichkeit bei billiger electricischer Kraft den Halbzellstoff durch die oxydierende Wirkung der Hypochlorite bezw. Von Chlor und Alkali auf die Inkrusten in Zellstoff zu verwandeln.

Das Aufschliessverfahren hat auch bei Holzabfällen nicht versagt. Aus "Schwartenholz" konnte Halbzellstoff in gleich

hoher Ausbeute wie aus üblichem Zellstoffholz hergestellt werden. Aber nicht nur Holz allein, auch Stroh udgl. (Schilf usw.) erfahren Aufschliessung. Es ist eine verhältnismässig geringfügige Abänderung des üblichen Aufschliessverfahrens mit Sulfiten, die zu den wie ich glaube, bemerkenswerten Ergebnissen geführt hat. Natürlich besteht auch die Möglichkeit durch modifizierte alkalische Verfahren Ähnliches zu erreichen. Einige solcher Verfahren sind ja schon in Patentschriften beschrieben worden. Sie alle werden dazu beitragen, dass der bisherigen Verschwendung von Holzmaterial in etwas Abbruch getan wird, indem nicht mehr 50–60% sondern weit weniger des Holzes in die Ablauge gehen werden, ein vom volkswirtschaftlichem Standpunkte aus hochbedeutsames Ziel.

## ANALYSE DU PAPIER (DOSAGE DES FIBRES)

PAR MR B. SETLIK, ING. CHIM.

*Prague, Austria*

Il est connu que lorsqu'on examine un papier sous le microscope certain réactif tels qu'une solution de iode dans de l'iodure de potassium et dans le iodure de zinc nous rendent des grand services en faisant distinguer les différentes fibres dont se compose le papier par la différence de coloration donnée aux fibres par les réactifs. Il est souvent très difficile de reconnaître les fibres d'après leur forme car elles sont dans le papier déchirées et déformées. J'ai trouvé qu'avec au peu d'expérience on peut reconnaître les différentes fibres du papier par les colorations diverses que donnent les dits réactifs et sans avoir recours au microscope; ce qui est très pratique. Cette methode donne en général de bons résultats; elle est très expeditive et pratique surtout lorsqu'on ne dispose pas d'un bon microscope ou en voyage lorsqu'on veut vite s'assurer de la composition du papier. Il est clair que lorsqu'il s'agit de papiers très compliqués, l'examen ne peut être fait sans l'aide du microscope. Si par hasard le papier contient de l'amidon il faut le traiter a l'eau chaude acidulée pour l'en débarrasser.

J'emploie les solutions, dont on se sert pour distinguer sous le microscope des différentes fibres par leur coloration au contact des dites solutions. Quoique la préparation de ces réactifs est connus je l'indique toute de même.

### I. Solution de iode au iodure de potassium.

|          |                     |
|----------|---------------------|
| Eau      | 20 cm. <sup>3</sup> |
| KI       | 2 gr.               |
| I        | 1,15 gr.            |
| Glycerin | 2 cm. <sup>3</sup>  |

II. Solution de iode au iodure de zinc et de potassium. On prépare d'abord une solution de 20 gr.  $\text{ZnCl}_2$  en 10 cm<sup>3</sup> d'eau, puis une solution de 2,1 gr. de KJ et 0,1 gr. I dans 5 cm<sup>3</sup> d'eau. On mélange laisse réposer et décante le liquid claire.



III. Solution de iode au chlorure de magnesium. 50 cm<sup>3</sup> une solution saturée de MgCl<sub>2</sub> et 2,5 gr. de la solution I.

IV. Solution de phloroglucine.

On dissout 1 gr. de phloroglucine dans 50 cm<sup>3</sup> d'alcool et on ajoute 25 cm<sup>3</sup> d'acide chlorhydrique.

Voici comme on procède pour obtenir des réactions. On fait tomber une goutte de la solution I et de la solution II sur le papier examiner et on laisse réagir chaque solution pendant 20-25 secondes, puis on lave avec de l'eau, en faisant tomber une goutte d'eau, puis on observe de quelle façon la tache change la couleur ou comment elle se décolore plus ou moins vite. La solution I réagit plus vite que la solution II. (La solution III ne s'emploie que lorsque les premières deux solutions ne suffisent pas à reconnaître la nature de la fibre.) Ainsi les chiffons se décolorent plus lentement que la cellulose.

Je me suis aussi occupé de fibres rarement employées chez nous et qui au Japon servent à la fabrication du papier qui est de plus en plus importé en Europe.

Lorsqu'il s'agit de papiers très compliqués avec diverses fibres, des déchets, etc.; il faut tout de même avoir recours au microscope mais ces cas sont rares et en général ma méthode permet de vite reconnaître la composition du papier. Si le papier contient de l'amidon il faut l'en débarrasser en le lavant à l'eau chaude acidulée légèrement à l'acide chlorhydrique. Il arrive aussi que deux sortes des fibres donnent la même réaction lorsqu'elles sont soumises au même réactif, il faut alors essayer un autre. J'ai examiné les réactions de papiers contenant les fibres suivantes: cellulose de bois crue et blanchie, cellulose de paille, esparto kodzu, misumata, gampi lin, coton, bois, bambou. Voici la liste de la coloration des taches faites sur ce papier examiné à l'aide des réactifs.

*Fibres simples.* Coloration avec la solution I + KI.

Le papier se colore *en brun violet*: Kodzu lavé avec de l'eau la couleur devient d'abord rouge, puis passe au bleu d'indigo.

Le papier se colore *en jaune brunâtre*: Misumata lavé devient olive puis jaune verdâtre. Gampi en peu plus foncé que misumata. Bambou lavé devient *jaune*. Pâte de bois se reconnaît aussi au phloroglucine.



Le papier se colore *brun tabac*: *Lin*, au lavage brun clair, les bords bleus. *Coton* au lavage devient bleu. *Cellulose* (blanchie) coloration olive pale puis decoloration complète. *Pâte de bois* (brune) après lavage violet sale.

Le papier se colore *brun rougeâtre*: *Cellulose* (brute) au lavage comme la cellulose blanchie. *Cellulose* de paille au lavage plus claire qui la cellulose de bois blanchie.

Le papier se colore *jaune clair*: *Pâte de bois pure*.

Le papier se colore *violet presque noir*: *Esparto* au lavage violet bleu foncé de petites taches noires qui persistent longtemps.

Réaction par la solution  $I = Zn\ I$ .

*Coloration violet brunâtre*: *Cellulose de bois blanchie*. *Cellulose de bois brute*. Les deux se décolorent très vite. *Cellulose de paille* se décolore plus lentement.

*Coloration bleu violet quelquefois très foncé*: *Kodzu* lavé passe au violet et devient *bleu* (cellulose et lin se décolore au violet claire) (lin et coton se décolore lentement). *Gampi* lavé passe au gris et se décolore complètement.

*Coloration violet rouge*: *Esparto* pâlit au lavage puis devient gris bleu avec les taches foncées.

*Coloration gris bleuâtre*: *Pâte de paille* se décolore en jaune très claire.

*Coloration gris brunâtre*: *Pâte de bois* (noir avec la phloroglucine).

Il est quelquefois difficile de distinguer deux espèces de fibres une à côté de l'autre, quelquefois on distingue facilement trois différentes fibres dans le papier selon leur espèce. Voici quelques exemples: Chiffons mêlés à la cellulose de bois. Plus il y a de chiffons plus la coloration avec  $I + IK$  (Solution *I*) est brun tabac foncé, si outre les chiffons le papier contient aussi la cellulose de paille la coloration est encore plus intense. Plus le papier contient des chiffons plus la décoloration est lente et teinté en oliv, ou en gris. S'il contient peu de chiffons la décoloration est brun rouge. On distingue le coton du lin à ce que le lin reste brun violet après le lavage, tandis que le coton devient et reste bleu, un peu olivâtre. Si les chiffons mixtes se trouvent avec de la cellulose il est difficile de les distinguer à moins ne soit en petite quantité. *Pâte de bois* et cellulose se colore en jaune-brun et se décolore en jaune claire

très vite, mêlé à des chiffons la couleur reste bleue. Les bord et le milieu de la tache deviennent olive. La présance de la pâte de bois se reconnaît à l'aide de la phloroglucine. Si avec la pâte de bois se trouve de la cellulose de bois brute ou obtient une coloration brune orange, qui après être lavé prend une teinte jaune: *Cellulose de bois et de paille* — Coloration brun-rouge, plus il y a de la cellulose de paille plus la coloration tire sur le rouge, qui après le lavage devient clair. Les fibres qui se trouve us dans les papier japonais se comportent ainsi. Kodzu et mitsumata se colorent en brun havanne; plus on moïn foncé quelquefois en brun très foncé. La décoloration est olive et partielement brune. Kodzu et mitsumata se color en brune, lavé devient vert jaunâtre. Lorsqu'on n'arrive pas a déterminer espèce de fibre au moyen de la solution  $I \text{ KI} + I$  on examine le papier au moyen de la solution  $(II)I \div \text{Zn I}$ . Par ce réactif les chiffons melés à la cellulose donnent coloration violet (*bleu*) foncé qu'au lavage passe au violet bleuâtre et reste violet clair a la fin. Pour les chiffons de coton la tache devient plus grise après la décoloration tandisque pour les chiffons de lin elle passe plutôt au violet. Le papier fait avec pâte de bois et cellulose blanchie devient violet et se décolore jusqu'à une teinte jaune-clair, s'il contient aussi des chiffons la couleur passe à l'olive au lavage. Kodzu et mitsumata se colorent en violet de fer (comme la laque d'alizarine au fer) et au lavage devien ent d'abord vert bleuâtre puis gris. Kodzu et gampi réunis donnent la même coloration. Gampi et mitsumata se colorent en violet-sale au lavege pour passer ensuite au violet-clair puis à la fin au gris bleuâtre. Voici la table des résultats des réactions obtenues sur des papiers fabriqués avec diverses matières premières.

| Espèce de fibre               | KI + I   | KI + I<br>après le lavage                          | ZnI + I                  | ZnI + I<br>après le lavage                         | Remarque                        |
|-------------------------------|--|--|--------------------------|--|---------------------------------|
| Cellulose de bois ordinaire.  | Coloration brune                                 | Passé à l'olive tirant ensuite sur le brun.        | Violet brunâtre          | Se décolore assez vite en passant d'abord au gris. |                                 |
| Cellulose de paille blanchie. | Rouge brune clair plus que la cellulose de bois. | Deviennent plus claires.                           | Violet                   | Deviennent grises puis se décolorent tout à fait.  |                                 |
| Cellulose de bois blanchie.   | Brun-rouge.                                      | Pâlit devient olive très clair.                    | Bleu-violet              | Se décolore assez vite en passant d'abord au gris. |                                 |
| Pâte de paille.               | Brune tirant un peu sur le rouge.                | Se décolore lentement devient brun-clair.          | Coloration grise.        | Se décolore vite en un jaune très clair.           |                                 |
| Pâte de bois.                 | Brun-clair jaunâtre.                             | Deviennent plus claires mais garde la même nuance. | Gris tirant sur le brun. | Deviennent jaunes claires (chamois).               | Coloration rouge au phlogluçin. |
| Pâte de bois brune.           | Brune.   | Deviennent plus claires.                           | Brun-violet foncé.       | Deviennent un violet pâle.                         |                                 |
| Bambou.                       | Jaune brunâtre.                                  | Passé au jaune franc.                              | Violet-gris bleu.        | Se décolorent tout à fait.                         |                                 |

| Espèce de fibre          | KI + I                                 | KI + I<br>après le lavage  | ZnI + I                                      | ZnI + I<br>après le lavage                           | Remarque |
|--------------------------|--|--|--|--|----------|
| Lin chiffons de lin.     | Brune.                                 | Brun-claire bords bleus.   | Violet-brunâtre.                             | Se décolore lentement.                               |          |
| Coton chiffons de coton. | Brune.                                 | Devient bleu.  | Violet-bleu.                                 | Se décolore lentement.                               |          |
| Kodzu.                   | Brune tirant sur le violet.            | Violet foncé, puis indigo.   | Violet-bleu foncé presque noir.              | Devient plus clair à la fin <i>bleu</i> .            |          |
| Gampi.                   | Brune havana plus foncé que mitsumata. | Olive puis vert jaunâtre claire.   | Violet franc foncé plus foncé que mitsumata. | Se décolore vite complètement.                       |          |
| Mitsumata.               | Brune havane.                          | Olive c o m e Gampi mais en se décolorant ne fournissent pas un si franc vert-jaune. | Violet bleuâtre.                             | Devient facilement violet-claire puis gris verdâtre. |          |
| Lin et coton.            | Brun foncé.                            | Bleu-violet.   | Violet.                                      | Reste bleu violet à la fin devient gris.             |          |

| Espèce de fibre                  | KI + I                               | KI + I<br>après le lavage  | ZnI + I   | ZnI + I<br>après le lavage                  | Remarque             |
|----------------------------------|--------------------------------------|--|---|---|----------------------|
| Coton et cellulose blanche.      | Se décolore très vite en brun-rouge. | Se décolore plus lentement que la cellulose même reste olive brunâtre. | Violet de fer comme la liqueur d'alizarine et de fer. | Se décolore en gris.                        |                      |
| Lin, coton et cellulose blanche. | Rouge-brune.                         | Bleu-brun violet.  | Violet.   | Bleu-gris.                                  |                      |
| Lin et cellulose blanche.        | Brun tabac foncé.                    | Passe au violet foncé et reste violet.                                 | Violet.   | Passe au violet bleu et reste violet clair. |                      |
| Chiffons et en peu de cellulose. | Brun tabac.                          | Bleu-violet.   | Violet.   | Bleu.                                       |                      |
| Chiffons et pâte de bois.        | Brun-rouge.                          | Devient clair le bord bleu.  |   |   | Rouge au phlogluçin. |
| Pâte de bois.                    | Jaune.                               | Jaune-clair.   |   |   | Rouge au phlogluçin. |
| Cellulose de bois ordinaire.     | Brunâtre.                            |  |   |   |                      |
| Pâte de bois.                    | Jaune.                               | Jaune-clair.   | Violet.   | Se décolore en jaune-clair.                 | Rouge au phlogluçin. |
| Cellulose blanche.               | Brunâtre.                            |  |   |   |                      |



| Es-<br>pèce de fibre   | KI + I                   | KI + I<br>après le lavage   | ZnI + I      | ZnI + I<br>après le lavage  | Remarque   |
|--|--------------------------|---|--------------|---|--|
| Cellulose chiffon.<br>Pâte de bois.                              | Jaune.<br>Brunâtre.      | Jaune-clair.  | Brunâtre.    | Passe à olive, puis<br>se décolore com-<br>plètement.                                     | Avec Mg. Cl <sub>2</sub><br>violet brun<br>lavé devient à<br>la fin jaune.<br>Mg. Cl <sub>2</sub> rouge. |
| Cellulose de bois.<br>Cellulose de paille.                       | Brun-rouge.              | Olive-claire.   |              |   |  |
| 10% chiffons.<br>90% cellulose.                                  | Brun-tabac.              | Devient olive brun<br>les bords bleu.                               | Violet.      | Bleu-clair.   |  |
| 20% chiffons.<br>80% cellulose.                                  | Brun-rouge claire.       | Passe à l'olive. On<br>remarque long-<br>temps des fibres<br>bleus. | Violet.      | Se décolore vite<br>mais toute de-<br>meine plus len-<br>tement que la<br>cellulose pure. |  |
| 95% chiffons.<br>5% cellulose.                                   | Brun tabac foncé         | Bleu-clair.   | Violet.      | Se décolore lente-<br>ment.   |  |
| 70% cellulose de<br>bois.<br>15% chiffons.<br>15% pâte de paille | Brun foncé vio-<br>lacé. | Bleu-violacé.<br>Reste longtemps.                                   | Violet pure. | Violet-bleuâtre.  |  |

| Esèce de fibre   | KI + I                    | KI + I<br>après le lavage                                 | ZnI + I      | ZnI + I<br>après le lavage | Remarque   |
|--|---------------------------|---|--------------|----------------------------|--|
| 50% chiffons.<br>15% cellulose de paille.<br>35% cell. de bois.    | Brun foncé presque noire. | Bleu franc.   | Violet foncé | Violet-bleuâtre.           |  |
| 30% chiffons.<br>15% cellulose de paille.<br>55% cell. de bois.    | Brun foncé.               | Bleu-sâle.  | Violet-brun. | Violet bleu puis gris.     |  |
| 50% cellulose.<br>50% chiffon.                                     | Brun-tabac.               | Se décolore lentement le autre olive les bords gris-bleu. | Violet.      | Gris-violacé.              |  |
| 45% cellulose de bois.<br>45% cellulose de paille.<br>5% chiffons. | Brun-violet.              | Jaune-claire.<br>Verdâtre.<br>Verdâtre.                   | Violet.      | Jaune-claire.<br>Verdâtre. | Par Mg. Cl <sub>2</sub> , rouge tirant sur brun, lavé devient jaune pur gris verdâtre. |

| Espèce de fibre   | KI + I                        | KI + I<br>après le lavage                          | ZnI + I        | ZnI + I<br>après le lavage  | Remarque               |
|---|-------------------------------|--|----------------|---|------------------------|
| 50% cellulose,<br>40% pâte de la.   | Brun-tabac.                   | C o u l e u r olive,<br>bords gris bleu-<br>âtres. | Violet de fer. | Gris-bleuâtre.  | Phloroglucin<br>rouge. |
| Papier d'alfa (es-<br>parto).   | Violet foncé<br>presque noir. | Violet blue indigo,<br>petites taches<br>noir.     | Violet-noir.   | Passé au bleu puis<br>gris les taches<br>indigo restent<br>longtemps. |                        |
| Papier Roneo $\frac{1}{3}$<br>chiffons, $\frac{1}{3}$ cellu-<br>lose de bois, $\frac{1}{3}$<br>esparto. | Brun-foncé.                   | Reste long-temps<br>brun puis olive<br>brunâtre.   | Violet foncé.  | Se décolore lente-<br>ment reste vio-<br>let brun taches<br>foncé.    |                        |
| Kodzu et mitsu-<br>mata.  | Brun-havane pur.              | Olive parci et par<br>la brun.                     | Violet de fer. | Verd bleuâtre à la<br>fin gris.                                       |                        |
| Kodzu et Gampi.   | Ainsi que précé-<br>dant.     |  |                |   |                        |

## BREEDING MAIZE FOR INDUSTRIAL PURPOSES

BY LOUIE H. SMITH

*Professor of Plant Breeding, University of Illinois,  
Urbana, Illinois*

No other agricultural crop is made to serve such a variety of purposes as Indian corn. The long list of products and by-products manufactured from the grain as well as from other parts of the plant is ever increasing. In view of this fact is suggested the idea of adaptation by altering the physical structure or the chemical composition, as the case may be, of the various plant parts involved in order to better serve the varied and special needs.

In those industries utilizing the grain, starch is of course usually the basic product sought. This starch is either refined and sold as such, or it is converted into some of its transformation products such as glucose, alcohol, gum, dextrin, etc. Upon first thought, therefore, one might suppose that a variety of corn high in starch content would be the most desirable kind for these industries. But the case is not so simple as would appear on first thought for with the great development of by-products in these industries within recent years conditions are entirely changed. For example, the protein compounds have found an important place on the market on account of the demand for these by-products for feed-stuffs. Perhaps the most striking development of such a by-product is the corn oil. In former years the germs which contain the bulk of the oil were a waste product. Now such is the demand for the oil of corn that this substance has become pound for pound much more valuable than the starch itself. According to present market reports corn oil is quoted as being worth more than three times as much as corn flour.

In view of these facts it will be seen that no one kind of corn will be suited equally well to all the corn industries but that each industry may demand a sort adapted to its own particular needs which indeed may even vary from time to time according to market demands.

It is interesting, therefore, in this connection to know in what manner and to what extent corn may be influenced as to its composition.

Sixteen years ago the Illinois Agricultural Experiment Station began some experiments to answer these questions. It was already established that the composition of grain could be affected to some extent by environment. The case of the sugar beet stood as a classic example of what might be accomplished in changing the composition of a plant part by directing the forces of heredity. So far as known, however, the matter of breeding to influence the composition of a grain by selection was a new proposition.

It was necessary, therefore, to work out first methods of selection and then plans for propagating the breeding plots.

In taking up the investigation it was proposed to take a variety of corn and to select in four different directions, as follows:

First, a strain was selected to increase the protein content, the practical consideration in this case being from the nutrition standpoint.

From the same original lot a second strain was selected for a low protein content. Low protein, of course, means high starch and in such a corn we would have theoretically a kind well adapted for distilling purposes.

In another strain high-oil content was the object sought, making of this a valuable corn for the glucose and allied industries in which the oil output forms such an important product.

Finally a low-oil strain was started chiefly for the purpose of comparison. Incidentally, however, a kind of corn with a reduced oil content would be of advantage in feeding hogs for the finest quality of bacon and lard.

The corn chosen for carrying out these experiments was an ordinary white variety grown in central Illinois and then known as "Burr's White." Its original composition was as follows:

|                     |       |
|---------------------|-------|
| Protein.....        | 10.92 |
| Oil .....           | 4.70  |
| Ash .....           | 1.43  |
| Carbohydrates ..... | 82.95 |



Selecting by chemical analysis those individual ears whose content was found to be best suited to the various purposes, and breeding in separate and isolated plots each group by itself, four strains were gradually evolved which have finally developed into quite different kinds of corn so far as chemical composition of the grain is concerned.

Naturally the results have been affected more or less by environmental agencies. Thus there have been fluctuations due in part to soil and season, which influences it has been impossible to entirely eliminate from those due to heredity.

In order to obtain a brief comprehensive view of what has been accomplished in these experiments up to the present time, perhaps we may best compare the analyses of the four strains in the crop of last year (1911), after 15 years of breeding, with the original variety in 1896 from which they emanated.

In doing so, however, we should bear in mind the above statement concerning seasonal fluctuations and consider that we have represented in these data the results of a single season which might have been slightly modified in another kind of a season.

Following are the results of the protein breeding:

#### PROTEIN CONTENT, DRY BASIS

|  |                |
|--|----------------|
| Original Variety, Crop of 1896 . . . . . | 10.92 per cent |
| High-Protein Strain, Crop of 1911 . .    | 13.78 per cent |
| Low-Protein Strain, Crop of 1911 . .     | 7.89 per cent  |

It may be noted here that the figures given above for the composition of the original variety represent fairly well the average composition of ordinary dent corn.

Since in the percentage composition protein and starch are complementary, it appears that we have now in this high-protein strain a sort of corn that contains about  $1\frac{1}{2}$  pounds less starch per bushel than ordinary corn, while the low-protein strain would furnish a corn about  $1\frac{1}{2}$  pounds per bushel richer in starch than average corn.

The progress in breeding to influence the oil content is shown in similar manner in the following results:

## OIL CONTENT, DRY BASIS

|                                     |               |
|-------------------------------------|---------------|
| Original Variety, Crop of 1896..... | 4.70 per cent |
| High-Oil Strain, Crop of 1911.....  | 7.51 per cent |
| Low-Oil Strain, Crop of 1911.....   | 2.05 per cent |

Thus we see that breeding has produced in the high-oil strain a kind of corn that now contains almost  $1\frac{1}{2}$  pounds per bushel more oil than exists in average corn, while on the other hand breeding for low oil has caused a reduction in this constituent amounting to about  $1\frac{1}{3}$  pounds per bushel. Since there exists a correlation between oil and protein this last strain is correspondingly richer in starch.

It may be said that these experiments are still being continued and it is possible that even wider limits may be reached in some directions. These results serve to indicate something of the possibilities for improvement along these lines.

Very little has been done in improving economic production in our corn industries through chemical control of the raw product. The sugar beet stands as the classic example of the adaptation of a plant by the strenuous control of its chemical composition. In Europe considerable attention is given to the adaptation of the potato with reference to its starch content for distilling purposes, and special stress is laid upon the matter of composition of barley in its application to the brewing and distilling industries.

Doubtless vast possibilities exist for improvement in economic production in our corn industries in this very matter of the adaptation of corn to meet the special requirements by breeding for special industrial purposes.

# THE CONSUMPTION OF CAUSTIC SODA IN COOKING WOOD AND THE INFLUENCE OF THIS CONSUMPTION ON THE YIELD AND BLEACHING PROPERTIES OF THE FIBRE PRODUCED

By E. SUTERMEISTER  
*Cumberland Mills, Maine*

In spite of the many years which have elapsed since the introduction of the soda process for cellulose manufacture, it is still run largely by rule-of-thumb methods. It is, for instance, known in a general way that increasing the time of cooking, the amount of caustic, or the steam pressure will diminish the yield, but the exact relation of these three factors has, so far as we have been able to discover, never been worked out. Another point on which no information was available was the consumption of caustic soda in cooking wood and the influence of this consumption on the yield and bleaching properties of the fibre produced. As it seemed desirable to obtain this information a series of cooks of poplar wood was made with this object in view.

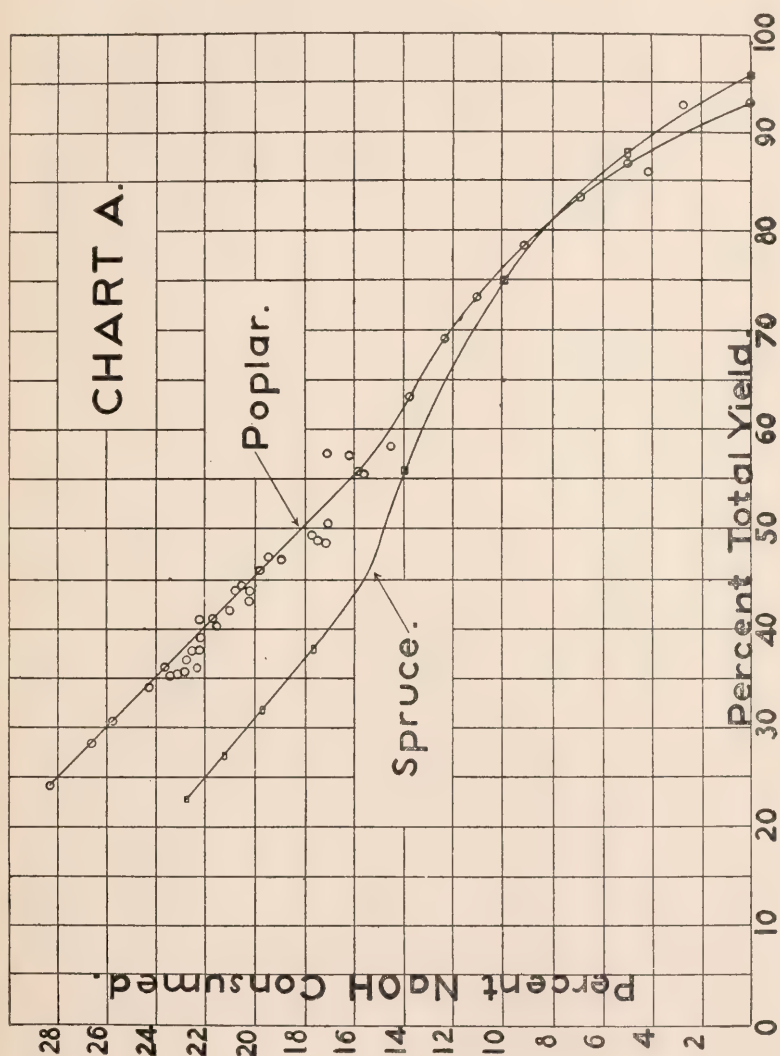
The wood used was in the form of the regular chips employed in pulp mill practice, and consisted almost entirely of two species of poplar, *Populus tremuloides* and *P. grandidentata*. The cooks were made in two ways; those in which less than 10% of caustic was used being digested at about 95° C. in a copper flask fitted with a reflux condenser, while those with over 10% of caustic were cooked in a small rotary digester heated by a gas flame. At the end of each cook the black liquor was sampled, the fibre washed and its yield carefully determined.

The black liquor was analyzed in the following way. To 300 cc. of water containing 15 cc. of barium chloride solution (400 grams per litre) there was added from a pipette 25 cc. of the black liquor. This was then titrated with normal acid and the end point determined by removing a drop at intervals and allowing it to fall into a thin layer of dilute phenolphthalein solution contained in a beaker. When the drop no longer produced a pink color the

reaction was considered complete. A second test was then made by evaporating 25 cc. of the black liquor to dryness, burning off the organic matter and titrating the soda ash present with normal acid, using methyl orange as an indicator. The relation of these two tests gives the causticity of the black liquor and by comparing this with the causticity of the original cooking liquor the amount of caustic used up in the process can be readily calculated.

The results of the entire series of cooks are shown in chart A in which the total yield, whether of good fibre or of merely softened chips, is plotted against the caustic consumed. Both of these are expressed in percentages based on the bone-dry wood used. The starting point of this curve is taken as the yield obtained when finely divided chips are extracted with water at 95° C. till the extract is colored only very faintly yellowish. This chart also shows a curve plotted in the same way from the results of a few cooks of spruce chips. It is seen that in a general way the reactions follow the same course, though the slight divergence of the upper portions of the curves seems to indicate that the celluloses being acted upon are different in their composition.

A study of the curve for poplar shows that between the points of 14 and 19.5% caustic soda consumption the relation between the yield and the caustic soda used up is not so definite as it is beyond these points. This may perhaps be due to the fact that within this range the transition from chips to fibre takes place while below 14% and above 19.5% it is practically all chips and fibre respectively. It is seen that the reaction taking place up to a consumption of 15% of caustic is quite different from that above this point. This probably indicates that in the first portion of the cook the non-cellulose constituents of the wood are being dissolved most rapidly, while after 15% of caustic has been used up the residue is as nearly pure cellulose as the process will yield and from this point on is dissolved as a whole. There is, then, little to be gained, so far as the purity of the product is concerned, by making the cooking conditions severe enough to use up more than 15% of caustic soda. It is, however, quite probable that the additional cooking would impart to the fibre certain desirable physical qualities which would not be in evidence in the less drastic cooks.





In each of the cooks in which the chips were sufficiently acted upon to produce fibre a study was made of its bleaching qualities in connection with the caustic consumed, the strength of the solution at the end of the cook and the percentage of residual caustic based on the bone-dry wood. It was expected that the bleach required would depend very largely on the amount of caustic consumed but it was proved that all three of the above factors could be varied within quite wide limits without appreciably changing the amount of bleach required. Thus fibre bleaching with about 7% of bleach was produced in cooks where the consumption of caustic varied from 20 to 25%, the residual caustic from 3.5 to 8%, and the strength of solution at the end of the cook from 8 to 22 grams per liter of caustic soda. It appears to hold true that a low consumption together with a slight excess of caustic will give a hard bleaching fibre while if the excess is greater the fibre will bleach easier even if the consumption of caustic is the same or slightly less.

It is highly probable that the bleaching properties of the fibre depend on certain definite combinations of the three factors mentioned, but the data available are not sufficient to determine positively the laws which govern the results.

In considering the curves shown on chart A it is to be noted that the points plotted were determined under very widely varying conditions of treatment. Thus the steam pressure has varied from 70 to 130 lbs., the caustic added from 22 to 50%, etc., yet the yield seems to be perfectly definite for any given consumption of caustic regardless of how this consumption was caused to take place. This fact, taken in connection with the slight variations in bleaching properties of fibre produced under such different conditions, leads to the conclusion that in the cooking of wood the important point is to use up a definite percentage of caustic and that so far as the character of the product goes it is apparently immaterial whether this consumption is caused by time, temperature, strength of cooking liquor or any other factor.

It should, therefore, be possible to ascertain the condition of the stock in the digester at any time by making an analysis of the black liquor, and thus avoid over-cooked or under-cooked fibre. The chief reason why this cannot be done at present is the

length of time necessary for the determination of the total soda in the black liquor. If a rapid and accurate method could be devised for this test it is thought that this manner of following the progress of the cook would prove very valuable in the soda process.

In conclusion I wish to acknowledge my indebtedness to S. D. Warren & Co., in whose laboratory this investigation was carried on, and to my associates for much valuable assistance in obtaining the original data.



### *Abstract*

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## ON THE CHEMICAL COMPOSITION OF WHITENED RICE, WITH ESPECIAL REFERENCE TO THE NUTRITIVE VALUE OF ITS PROTEIN MATTERS FOR SAKE YEAST AND ASPERGILLUS ORYZAE

BY TEIZO TAKAHASHI AND HISAE SATO  
*Brewing Experiment Institute, Tokyo, Japan*

The chemical analyses of whitened rice hitherto published have, in all the cases, been limited to those made upon ordinary samples. The authors have analyzed samples of rice which were specially prepared for the purpose of brewing saké, namely, those which were whitened in the highest degree. They were 44 in number and collected from 22 breweries, which are located in different parts of Japan.

After determining the general chemical composition of these samples and discussing the results, the authors proceed to the examination of protein matters, of which they have isolated albumin, globulin, prolamin and oryzenin. The existence of prolamin, a protein with bitter taste and soluble in 80% alcohol, in rice is worthy of remark, inasmuch as Rosenheim and Kajiura, in their examination of rice, failed to detect any protein soluble in alcohol, and Osborne states that the absence of prolamin in rice is an exception to the general rule that all the cereals examined in his laboratory contain prolamin. There is, therefore, reason to doubt the correctness of the observations made by Rosenheim and Kajiura. Elementary analyses of the proteins thus isolated from rice showed, however, small differences in their composition as compared with the composition of those contained in other cereals and determined by Osborne, Ritthausen, Chittenden and others, the essential differences in the case of prolamin being that the percentage amount of nitrogen in the protein obtained from rice is somewhat below that contained in other cereals.

Further, the authors have examined the nutritive values of the four proteins obtained from rice for saké yeast and *Aspergillus Oryzae*, and the results show that the albumin, the globulin and the orizenin are all and equally well assimilated by these organisms whilst the prolamin is not in the least utilized by them.



# THE CARBOHYDRATES OF WHEAT AND WHEAT PRODUCTS AND CHANGES IN SAME DURING DEVELOPMENT OF THE GRAIN

BY GEORGE L. TELLER  
*Chicago, Ill.*

During the summers of 1897 and 1898, while the writer was chemist of the Arkansas Agriculture Experiment Station at Fayetteville, Arkansas, he collected samples of wheat on each succeeding day from the first formation of the grain until several days after it was ripe and fit for harvesting. The purpose of collecting these samples was to determine changes in composition both with regard to the nitrogenous matter and the other constituents. Determinations as to the composition of the nitrogenous matter were made on each individual sample of wheat collected. For the other determinations the cuttings of each three days were mixed and the analyses were made on these mixtures. The mixtures are designated by groups in numerical order. Groups V and VI represent the wheat in the milk when gathered, — Group X at about the average time of cutting.

The results of the first year's work were published in detail in Bulletin No. 53 of the Arkansas Agriculture Experiment Station in September, 1898. The results of the second year's experiments have not previously been published. Much of the analytical work for the latter experiments was completed by Mr. J. F. Moore and supplied to the writer after he had left the Experiment Station in 1899. The analyses of flour, germ and bran were made recently at The Columbus Laboratories, Chicago.

There are three distinct parts of the wheat grain, — the bran, the embryo or germ, and the endosperm or portion which yields the flour. During the milling operations in most mills the germ and bran, with some portion of the endosperm, find their way together into the offal which is usually sold as feed for animals. In some of the larger mills the germ is separated in a nearly pure condition so that with a little care it can be obtained in a fair de-

gree of purity. The sample of germ of which the analysis is here given was freed as completely as possible from flour and bran and was fairly pure. It contained, however, some flour which was pressed into it during the process of flattening the germ in the milling operation. This accounts, at least in part, for the starch found in it. Patent flour, such as was used in this series of analyses, contains neither bran nor germ. The starch in the bran comes largely, if not entirely, from flour which was not removed during milling.

There is a distinct connection between the composition of the three parts of the wheat berry and the composition of the wheat at different periods of its growth because there is a marked difference in the rate of development of the different parts of the wheat berry in the process of its growth. Especially is this true concerning the bran and endosperm, for the proportion of bran to endosperm is much greater in the smaller and immature kernels than in the fully ripened and plump grain.

The method of analysis used for the determinations on the carbohydrates is given below. The method of determining the other constituents is the same as outlined in the official methods for food analyses, excepting that the amides were determined by precipitating all proteids and albuminous matter from the water extract by the use of phosphotungstic acid and determining the amide nitrogen in the solution. This method has been found to be preferable to the use of cupric hydroxide, for wheat products. In the table of analyses the actual proteins are given and were obtained by multiplying the actual protein nitrogen by the factor 5.7, which is the true factor for wheat proteids. The amides were found by multiplying the amide nitrogen by the factor 5. This factor is based on the average composition of the amides, asparagine and glutamine. For convenience of reference both the total and amide nitrogen are also given in the table.

Pentosans: These were estimated by the current method of the Association of Official Agricultural Chemists, which is distilling with hydrochloric acid to convert them into furfural, precipitating the furfural with phloroglucin and computing the results as xylan.

Sugars: To determine the sugars, two grams of meal were

extracted with hot, strong alcohol. This was distilled off and the sugar extracted from the residue with water. In the solution thus obtained the reducing sugar was determined by Allihn's method. In another similar extract the total sugar was determined by inverting the sucrose in the water solution with hydrochloric acid, neutralizing the acid with sodium carbonate and then proceeding as before. The difference in the reducing power of the extract before and after inverting gave figures for computing the sucrose.

**Starch:** The hot alcohol extracts not only the sugars, but also the greater part of the fat. The residue is therefore in a suitable condition for determining the starch by the diastase method. This method was carried out according to details adopted by the Association of Official Agricultural Chemists, except that instead of boiling the acidified solution for two and one-half hours the flasks containing the liquid were immersed in a steam bath for three hours. The temperature in this bath was very nearly that of boiling water, and the method has been found convenient and satisfactory. The resulting sugar was determined by Allihn's method. The results include starch and dextrins. The dextrins being determined, the starch is found by difference.

**Dextrins:** It was found that extracting the meal with hot 92 per cent alcohol converts a portion of the starch into a form soluble in cold water and a separation of the dextrin from this portion of material is impracticable. Accordingly, to determine the dextrins, five grams of the fresh material were thoroughly digested in a 250 cc. flask with cold water; 200 cc. of this clear filtered extract were treated with hydrochloric acid in the steam bath in the same manner as the diastased starch solutions. The reducing power of the resulting solution is due to sugars and dextrins. The reducing power of the sugar having been determined, the dextrin compounds are computed from the difference.

In the tabulated results of the series of analyses on wheats out at different dates, the amount of starch and undetermined is given as found by difference. No determination was made of the actual amount of starch present in this series, but in the preceding year a determination was made of the starch by the diastase method. At that time there was found to be a close agreement

between the starch as found by difference and as determined by analysis over the latter part of the series, but over the first part of the series the difference was appreciably greater than the amount of starch found. This latter condition is apparent with regard to the results obtained on the bran and germ. It is possibly due to a part of the pentosans being of a higher molecular weight than xylan, but no effort has been made to determine clearly upon this point.

With regard to the flour, the starch is in excess of the difference as found. Several determinations were made on sugars and starches by the method used in determining pentosans, with results as follows:

|                                 |       |
|---------------------------------|-------|
| Commercial corn sugar           | .74%  |
| Merck's pure anhydrous dextrose | 1.2%  |
| Wheat starch                    | 1.48% |

It is probable that the greater part, if not all, of the apparent pentosans found in flour are from some other product. It is known that certain pentosans are derived from the nucleins of wheat, and since germ is rich in nucleins a part of the pentosans obtained from the germ would naturally be derived from the nucleins. It is possible also that some of the pentoses obtained from bran are derived from the same body. The amount of dextrin, sugar and starch in the sample of commercial bran examined is less than 30 per cent while the amount of crude fiber and pentosans is 35 per cent. Neither of these two latter substances serves any great purposes as an article of food. Their amount in pure bran would be in excess of what is found in this sample of commercial bran and it thus becomes apparent that the greater part of the carbohydrates in pure bran is of very little food value.

There is a marked difference in the amount of cane sugar in the germ, the bran and the flour, while reducing sugars are found in none of them, or at least they are not present in quantities greater than a trace. Dextrins are present to a considerable extent in the flour and also in the germ. It is quite certain that the amount in flour will vary with the condition of the grain when it was milled.



It is interesting to note that no reducing sugars were found in any of the samples of fully matured wheat, but that there is an appreciable quantity in the very immature grain. There is also a distinct falling off in the amount of sucrose, of dextrose, of pentosans, and in fact of all substances excepting starch as the grain becomes more mature. The amount of amides in the very immature grain is large, as is expected, for this is the form in which nitrogenous bodies are transferred from the stem of the wheat into the grain.

#### PROXIMATE COMPOSITION OF CERTAIN WHEAT PRODUCTS

|                               | Patent Flour<br>Per cent | Germ<br>Per cent | Bran<br>Per cent |
|-------------------------------|--------------------------|------------------|------------------|
| Moisture.....                 | 12.50                    | 7.80             | 11.80            |
| Ash.....                      | .40                      | 4.70             | 5.00             |
| Actual Protein.....           | 11.23                    | 25.87            | 14.65            |
| Amides.....                   | .15                      | 2.65             | .95              |
| Fat.....                      | 1.38                     | 11.40            | 3.80             |
| Crude Fiber.....              | .10                      | 1.35             | 11.30            |
| Pentosans.....                | 2.60                     | 4.90             | 23.73            |
| Dextrins.....                 | 5.53                     | 7.00             | 1.85             |
| Dextrose.....                 | trace                    | trace            |                  |
| Sucrose.....                  | .35                      | 14.60            | 4.60             |
| Starch and undetermined.....  | 65.76                    | 19.73            | 22.32            |
|                               | 100.00                   | 100.00           | 100.00           |
| Starch found by analysis..... | 68.75                    | 13.72            | 16.30            |
| Total nitrogen.....           | 2.00                     | 5.07             | 2.76             |
| Amide nitrogen.....           | .03                      | .53              | .19              |

TABLE SHOWING THE PROXIMATE COMPOSITION OF WHEAT, IN PER CENT OF THE AIR-DRY MATTER, AT THIRTEEN DIFFERENT PERIODS OF THREE DAYS EACH FROM THE SETTING OF THE GRAIN TO PAST RIPENESS, THE WHEAT BEING GATHERED AND DRIED ON THE STRAW

|                              | I<br>Per cent | II<br>Per cent | III<br>Per cent | IV<br>Per cent | V<br>Per cent | VI<br>Per cent |
|------------------------------|---------------|----------------|-----------------|----------------|---------------|----------------|
| Moisture.....                | 6.75          | 13.50          | 13.00           | 13.60          | 15.00         | 14.50          |
| Ash.....                     | 6.83          | 5.47           | 3.80            | 2.84           | 2.48          | 2.24           |
| Actual Protein.....          | 11.34         | 15.39          | 14.36           | 12.31          | 11.74         | 12.25          |
| Amides.....                  | 10.85         | 3.30           | 1.15            | .75            | .60           | .50            |
| Fat.....                     | 14.64         | 4.54           | 3.02            | 2.49           | 2.37          | 2.42           |
| Crude Fiber.....             | 9.91          | 8.90           | 6.33            | 4.41           | 3.71          | 3.22           |
| Pentosans.....               | 12.46         | 13.09          | 11.72           | 10.37          | 9.20          | 8.19           |
| Dextrins.....                | 6.80          | 3.84           | 2.70            | 2.60           | 2.14          | 2.30           |
| Dextrose.....                | 1.69          | .62            | .23             | .10            | .08           | .06            |
| Sucrose.....                 | 3.12          | 2.68           | 2.60            | 1.78           | 1.58          | 1.50           |
| Starch and undetermined..... | 15.61         | 28.67          | 41.09           | 48.75          | 51.10         | 52.82          |
| Total nitrogen.....          | 4.16          | 3.36           | 2.75            | 2.31           | 2.18          | 2.25           |
| Amide nitrogen.....          | 2.17          | .66            | .23             | .15            | .12           | .10            |



|                          | VII<br>Per cent | VIII<br>Per cent | IX<br>Per cent | X<br>Per cent | XI<br>Per cent | XII<br>Per cent | XIII<br>Per cent |
|--------------------------|-----------------|------------------|----------------|---------------|----------------|-----------------|------------------|
| Moisture . . . . .       | 14.65           | 15.20            | 15.35          | 15.20         | 14.75          | 14.80           | 15.00            |
| Ash . . . . .            | 2.12            | 2.15             | 2.10           | 1.94          | 1.94           | 2.06            | 2.07             |
| Actual Protein . . . . . | 12.37           | 12.37            | 12.08          | 12.25         | 12.19          | 12.08           | 12.14            |
| Amides . . . . .         | .50             | .40              | .40            | .40           | .40            | .40             | .35              |
| Fat . . . . .            | 2.36            | 2.49             | 2.41           | 2.40          | 2.50           | 2.43            | 2.57             |
| Crude Fiber . . . . .    | 2.93            | 2.93             | 2.80           | 2.77          | 2.69           | 2.81            | 2.87             |
| Pentosans . . . . .      | 7.85            | 7.86             | 7.53           | 7.40          | 7.85           | 7.38            | 7.43             |
| Dextrins . . . . .       | 2.65            | 2.50             | 2.72           | 2.69          | 1.74           | 2.46            | 2.46             |
| Dextrose . . . . .       | .07             | .05              | trace          | —             | —              | —               | —                |
| Sucrose . . . . .        | 1.25            | 1.40             | 1.34           | 1.24          | 1.34           | 1.46            | 1.46             |
| Starch and undetermined  | 53.25           | 52.65            | 53.27          | 53.70         | 54.60          | 54.12           | 53.65            |
| Total Nitrogen . . . . . | 2.27            | 2.25             | 2.20           | 2.23          | 2.22           | 2.20            | 2.20             |
| Amide Nitrogen . . . . . | .10             | .08              | .08            | .08           | .08            | .08             | .07              |

# TESTS TO DETERMINE THE COMMERCIAL VALUE OF WOOD PRESERVATIVES. A PROGRESS REPORT

BY HOWARD F. WEISS

*Assistant Director, Forest Products Laboratory, Madison, Wis.*

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## ACKNOWLEDGMENTS

The author wishes to acknowledge the services rendered by the following members of the Forest Products Laboratory who performed the experiments herein described: F. M. Bond, in charge of Wood Preservation; L. F. Hawley, in charge of Chemistry and Distillation; C. H. Teesdale, Engineer in Forest Products; Ernest Bateman, Chemist in Forest Products; C. J. Humphrey, Pathologist, Bureau of Plant Industry.

Acknowledgment is also made to Ira H. Woolson, Consulting Engineer, the National Board of Fire Underwriters, for his very courteous and valuable assistance in the inflammability tests.

## INTRODUCTION

A list of the various substances that have been used or suggested for preserving timber from decay would embrace many of those known to industrial chemistry. By-products for which no use could be found have generally taken their last stand as possible preservatives of wood. We have had sent to us for tests the condensed fumes of smelters, the waste liquors of pulp plants, the refuse of tanneries, the skimmed milk of creameries, and miscellaneous assortments of compounds under trade names. Many of these have been culled without any test whatever because the claims made for them were manifestly impracticable. Those, however, which appeared meritorious, or about which numerous inquiries from various consumers were received, were admitted to test.

The object of the tests here described is primarily to obtain information on the practical value as wood preservatives of those compounds or chemicals which fall within this latter classification,

so that intelligent replies might be given to the various inquiries received. Further, it was thought that such an investigation would show clearly the deficiencies of present practice and pave the way for increasing its efficiency, by suggesting lines for original research.

From 40 to 90 per cent, or an average of about 70 per cent, of the total cost of treating wood is in general due to the preservative alone. The most promising field for decreasing the cost, therefore, lies in decreasing the cost of the preservative used. In ordinary treatments with coal-tar creosote it is common practice to inject approximately ten pounds of the oil per cubic foot of wood, although about one-fifth of a pound will prevent fungous growth; in other words, a factor of safety of about fifty applied to the entire volume of wood is used. The safe reduction of this factor offers one of the many interesting problems.

Before undertaking investigations with new compounds, or improved methods of handling the old ones, it was thought best to first collect certain pertinent data which would be of most immediate value and which would broaden the investigator's viewpoint. The tests here described comprise what has been accomplished thus far and should, therefore, be considered simply as preliminary to the more serious problems involved.

#### PROPERTIES INVESTIGATED

The practical value of a preservative depends very largely upon the conditions under which it is used, and, as these vary considerably, the investigations must necessarily be broad. With this in view, and with a study of the inquiries received as a basis, the following points were studied in these tests:

1. The important chemical and physical properties of the preservative.
2. The effect of the preservative on the strength of the wood treated with it.
3. The ability of the preservative to penetrate and diffuse through wood.
4. The permanency of the preservative after its injection into wood. This involves a study into its volatility and leachability.
5. The combustibility of the wood treated with the preservative.

TABLE I

| PIECE NO | SIZE   | LATER CUT INTO       |   |
|----------|--|----------------------|---|
|          |  | PIECE NO (MARK)      | SIZE  |
| 1        | $1\frac{1}{4} \times 1\frac{1}{4} \times 13$ | 1-1<br>1-2           | $1\frac{1}{4} \times 1\frac{1}{4} \times 3$                 |
| 2        | "  | 2-1<br>2-2           | "   |
| 3        | "  | 3-1<br>3-2           | "   |
| 4        | "  | 4-1<br>4-2           | "   |
| 5        | "  | 5-1<br>5-2           | "   |
| 6        | "  | 6-1<br>6-2           | "   |
| 7        | $1\frac{1}{4} \times 2 \times 13$            |                      |   |
| 8        | "  |                      |   |
| 9        | "  |                      |   |
| 10       | "  |                      |   |
| 11       | $1\frac{1}{4} \times 1\frac{1}{4} \times 13$ | 11-1<br>11-2<br>11-3 | $1\frac{1}{4} \times 1\frac{1}{4} \times 4$<br>"<br>"       |
| 12       | "  | 12-1<br>12-2<br>12-3 | "<br>"<br>"   |
| 13       | "  | 13-1<br>13-2<br>13-3 | "<br>"<br>"   |
| 14       | "  | 14-1<br>14-2         | $1\frac{1}{4} \times 1\frac{1}{4} \times 6\frac{1}{2}$<br>" |

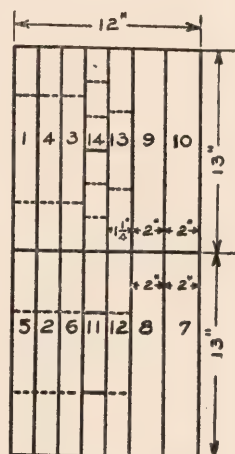


FIGURE I

| RECUT INTO      |   |
|-----------------|---|
| PIECE NO (MARK) | SIZE  |
| 14-1-1          | $1\frac{1}{4} \times 1\frac{1}{4} \times 2$ |
| 14-1-2          | "   |
| 14-1-3          | "   |
| 14-2-1          | "   |
| 14-2-2          | "   |
| 14-2-3          | "   |

6. The toxic efficiency of the preservative in inhibiting the growth of wood-destroying fungi.

7. The corrosive action of the preservative on steel.

8. The effect of the preservative on paint applied to the wood subsequent to treatment.

Since the investigations were started two other groups of inquiries have become apparent; namely, the effect of the preservative as an *electrolyte* and in *contaminating drinking water*. No systematic tests on either have, however, been made, nor any tests which pertain to a special or limited use.

#### METHODS OF TEST

The methods by which the various tests were conducted will be only briefly described.

Thoroughly air-seasoned eastern hemlock (*Tsuga canadensis* L.) was selected as the wood best suited for the tests because of its low inherent resistance to attack by fungi, its comparative uniformity of treatment, and its accessibility. Only perfectly clear, straight-grained, and uniform material, free from all mechanical and physical defects, was used; this being cut into test pieces 12" x 13" x 1 $\frac{1}{4}$ " and recut as shown in Figure 1 and Table 1.

#### *Chemical and Physical Properties of the Preservatives*

Under this heading were tested, by standard methods, the chemical composition of the preservative, its specific gravity, viscosity, odor, flash, and burning points. In all distillations the apparatus described in Forest Service Circular 112 was used.

The specific gravity was determined chiefly by a hydrometer or by a Westphal balance. Viscosities were obtained by using the Engler orifice viscosimeter at various temperatures. The flash and burning points were tested by heating the preservative at a rate of 2° C. per minute in an open flash-point tester, passing a small flame over the surface every minute.

#### *Injection of the Preservative*

Pieces Nos. 4, 5, 6, 7, 11, 12, 13, and 14-2 were injected with the preservative. Before injection they were oven-dried at 100° C., when they were weighed, and impregnated in the cylinder shown in Figure 2. The simplest procedure (Bethell process) was followed. For example: After the wood was placed in the cylinder the preservative was admitted, displacing the air, until the cylinder was completely filled; a hydrostatic pressure of about 50 pounds per square inch was then applied until the desired absorption was obtained, when the specimens were removed and



weighed within 24 hours; when necessary higher pressures were used.

### *Strength Tests*

Pieces 1, 2, 3, 4, 5, and 6, the latter three treated with the preservative, were tested in bending to failure in an ordinary 30,000-pound testing machine, using a center load over a 12-inch span. Care was taken to have all specimens at approximately the same moisture content at the time of test (about 6 per cent).

### *Penetrance of the Preservative into Wood*

Sticks 4, 5, and 6, after the strength data had been obtained on them, were split and the depth and character of the penetration recorded. This could usually be done visually, but with those preservatives which in aqueous solution were colorless, an aniline dye was used or the specimens were chemically analyzed.<sup>1</sup>

The results from these tests were used to supplement those secured from pieces 8, 9, and 10, which were tested in a specially constructed penetrance apparatus (see Fig. 3) operated as follows: A hole, one inch in diameter, was bored in the center of each stick (*E*) to a depth of three-fourths inch. The stick was then raised to a temperature of about 180° F. and clamped between two iron discs (*F* and *F'*) so that the preservative could be forced into the hole under a constant pressure and temperature. For oils the length of the pressure period was 30 minutes, and for water-soluble salts, 3 minutes, with the exception of sodium silicate, for which the time was prolonged to 30 minutes. The time it took to penetrate the wood longitudinally was noted, after which the specimen was sawed longitudinally and transversely through the center lines and the penetration radially, tangentially, and longitudinally was studied.

### *Volatilization Tests*

The volatility tests were made on oils only. Within three hours after stick 12 had been impregnated it was recut into three pieces each  $1\frac{1}{4}'' \times 1\frac{1}{4}'' \times 4''$  in size, weighed separately, and placed in the

<sup>1</sup> It was found by repeated tests that water and the dye had a tendency to penetrate in some cases slightly farther than the preservative, although the difference was of no practical significance.

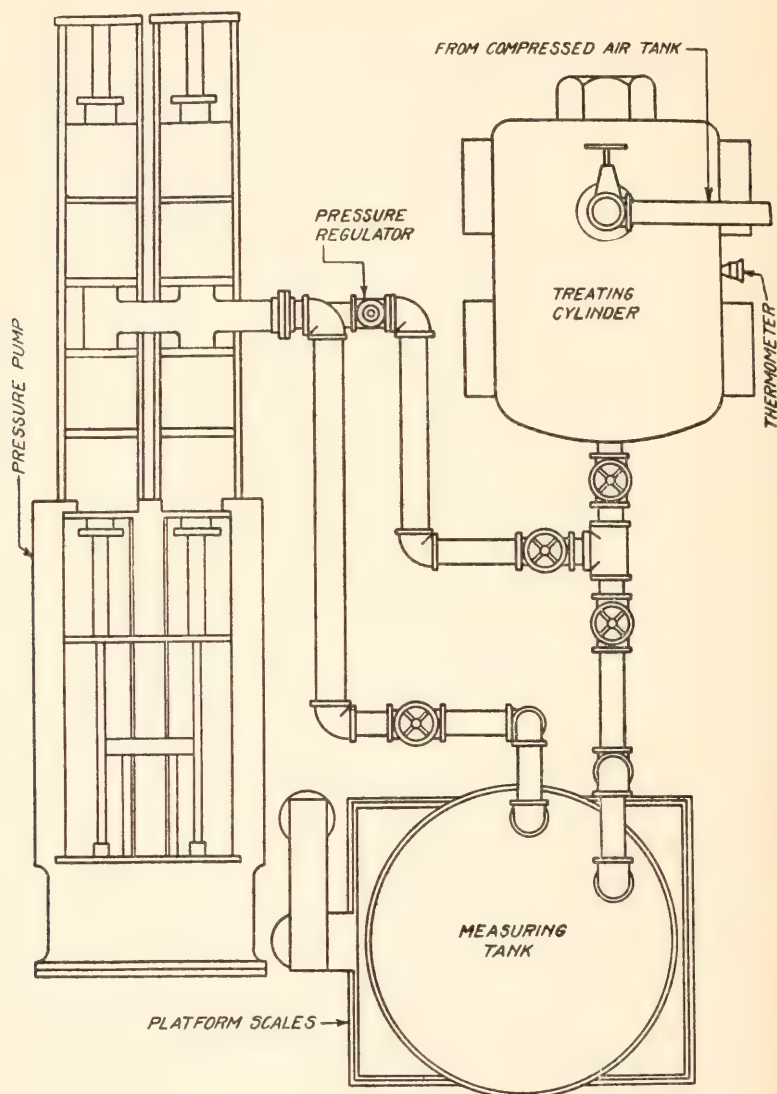


Figure 2. IMPREGNATION APPARATUS

volatility apparatus (see Fig. 4), which consists of an air-tight, metal box, 15" x 24" x 30", through which a constant current of air previously dehydrated by passing through sulphuric acid was passed. The box was heated to 30° C. by electric lamps, the temperature being automatically controlled within 1° C. The treated specimens were removed and weighed at weekly periods for three months. The loss in weight was taken as representing the amount of the preservative volatilized.

### *Leaching Tests*

Leaching tests were made on the water-soluble salts only. Within three hours after stick 13 had been impregnated it was recut into three pieces, each  $1\frac{1}{4}$ " x  $1\frac{1}{4}$ " x 4" in size, and weighed separately. Generally, within 48 hours of impregnation these pieces were submerged in a glass jar containing 300 cc. of distilled water at room temperature; this water was changed at stated intervals and analyzed for the presence of preservative. The total time of leaching was four weeks. To check the amount of the preservative remaining in the wood after the total submersion, the specimens were shredded and chemically analyzed.

### *Inflammability Test*

The crib and shaving tests ordinarily used in examining the combustibility of wood were all discarded because of inability to get sufficiently concordant results. This made it necessary to develop original apparatus (see Fig. 5) which consisted of a silica tube, wrapped with nichrome ribbon. An iron tube fitted with a mica sight was cemented below the silica tube.

The specimen of wood, after being lowered in the silica tube, was heated at a uniform rate, by passing twenty-four amperes of electric current through the nichrome ribbon. Temperature readings were obtained from a thermocouple placed beside the specimen and reading direct from a Hoskins pyrometer. A pilot light was used to ignite the gases distilled from the wood. Compressed air partially dehydrated by expansion was passed through the apparatus, its intensity being indicated by a sensitive liquid manometer. Three untreated test specimens were burned as a check against the three treated specimens. When the preservative was

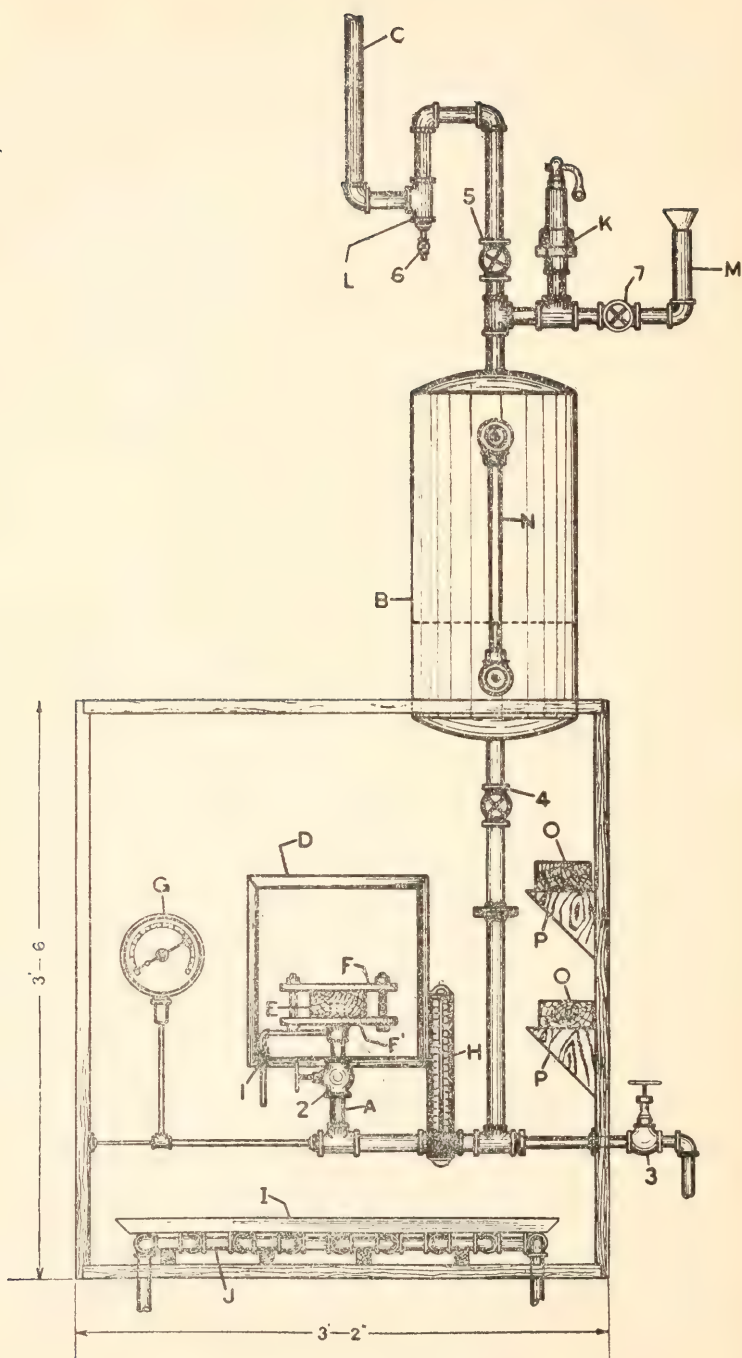


Figure 3. PENETRANCE APPARATUS

a water-soluble salt, the test specimens were first air-dried and then oven-dried before ignition. When the preservative was an oil, one inflammability test was made within twenty-four hours after impregnation and another after three months' seasoning in the volatility apparatus.

### *Toxicity Tests*

Because of the importance of toxicity tests and the inherent objections to various established methods of testing, three methods were followed:

1. Petri-dish method, in which the culture medium was made of juice from one pound of beef, 25 grams Löfflund's malt extract, 20 grams agar-agar, and 1000 cc. of distilled water.

2. The injection of the preservative into wood with a subsequent exposure to an isolated fungus (*Fomes annosus*) Fr. in sterilized jars.

3. The injection of the preservative into wood with subsequent exposure to various fungi in a fungus pit. Only those fungi which were known to attack wood substance were used.

At present, degrees of decay are determined visually. This method permits of too great error due to the personal equation. To overcome this the extent of attack in these tests was determined by noting the loss in weight of the wood after infection and by forcing a steel ball into it before and after decay, recording the force required to sink the ball to its semi-diameter.

### *Corrosion Tests*

To determine the corrosive action of the preservative on steel a strip of flange steel of the quality specified by the American Society for Testing Materials, August 16, 1909, was submerged in the preservative and heated to a constant temperature of about 98° C. The preservative was changed every week for four weeks in the case of oils; with aqueous solutions it was changed every day for one week. The difference in the weight of the steel before and after submersion was taken to indicate its corrosion. All depositions on the surface of the metal were removed as nearly as possible with a rubber policeman each time the preservative was changed. At the end of the test, where electrolytic deposition of metal had taken place, the deposited metal was removed by acid



TABLE 2.—CHEMICAL AND PHYSICAL PROPERTIES OF THE PRESERVATIVES

| Preservative<br>Designated by<br>Co-operator as | Specific<br>Gravity | Degrees<br>C. | Flash<br>point<br>°C. | Burning<br>point<br>°C. | Viscosity (Temperature °C.) |        |       |       | Odor                         | Remarks   |
|---|---------------------|---------------|-----------------------|-------------------------|-----------------------------|--------|-------|-------|------------------------------|---|
|   |                     |               |                       |                         | 10                          | 50     | 30    | 95    |                              |   |
| Coal-tar creosote                               | 1.048               | 60            | 93                    | 100                     | 3.1                         | 1.7    | 1.4   | 1.1   | Strong creosote              | Graded as "C"   |
| Coal-tar creosote<br>Frac. 1                    | .934                | 60            | 62                    | 69                      | ....                        | 1.1    | 1.0   | .95   | Like toluene                 | Includes oils distilling between<br>0—205° C.   |
| Coal-tar creosote<br>Frac. 2                    | 1.003               | 60            | 79                    | 85                      | ....                        | ....   | ....  | 1.0   | Strong like naphthalene      | Includes oils distilling between<br>205—250° C. Solid at room<br>temperature.                         |
| Coal-tar creosote<br>Frac. 3                    | 1.045               | 60            | 103                   | 110                     | 2.45                        | 1.4    | 1.2   | 1.1   | Strong coal-tar<br>creosote  | Includes oils distilling between<br>250—295° C.   |
| Coal-tar creosote<br>Frac. 4                    | 1.088               | 60            | 130                   | 136                     | ....                        | ....   | 1.51  | 1.11  | Mild coal-tar<br>creosote    | Includes oils distilling between<br>295—320° C. Would not<br>flow at 30° C.                           |
| Coal-tar creosote<br>Frac. 5                    | 1.150               | 60            | 172                   | 178                     | ....                        | ....   | 80.0  | 2.6   | Mild coal-tar<br>creosote    | Includes residue above 320° C.  |
| S.P.F. carbolineum                              | 1.127               | 16            | 133                   | 157                     | ....                        | 4.4    | 2.3   | 1.25  | Tarry (mild)                 | { These compounds are similar<br>in many respects. Their ex-<br>act composition was not<br>determined |
| Avenarius "                                     | 1.126               | 16.5          | 139                   | 166                     | ....                        | 7.5    | 2.4   | 1.25  | Tarry                        |   |
| C. A. Wood preserver                            | 1.195               | 60            | 90                    | *                       | ....                        | 17.5** | 6.3** | 1.4** | Disagreeable<br>pyroligneous | *Water boiled off preventing<br>burning   |
| Hardwood tar                                    |                     |               |                       |                         |                             |        |       |       |                              | **Viscosity orifice viscometer  |
| Wood creosote<br>(Douglas fir)                  | 1.052               | 60            | 45                    | 85                      | ....                        | 15.2   | 4.9   | 1.4   | Disagreeable                 | This resembled a tar more than<br>a "creosote"  |
| 1.07 oil  | 1.058               | 60            | 48                    | 65                      | 16.0                        | 3.7    | 2.0   | 1.2   | pyroligneous                 | A water-gas-tar product   |
| Timberasphalt                                   | 1.063               | 60            | 240                   | 260                     | ....                        | ....   | 99.2  | 5.2   | Like kerosene                | A residuum of petroleum   |
| Copperized oil                                  | .937                | 25            | 125                   | 164                     | ....                        | 18.0   | 5.1   | 1.5   | Like " (mild)                | Contains .34% copper  |
| Fuel oil  | .87                 | 60            | 72                    | 101                     | 2.8                         | 1.57   | 1.3   | 1.1   | Like " (strong)              | A crude petroleum   |

TABLE 2. CHEMICAL AND PHYSICAL PROPERTIES OF THE PRESERVATIVES. (Continued)

| Preservative<br>Designated by<br>Co-operator as | Specific<br>Gravity | Degrees<br>C. | Flash<br>point<br>°C. | Burning<br>point<br>°C. | Viscosity<br>(Temperature °C.) |    |    |    | Odor     | Remarks                                      |
|---|---------------------|---------------|-----------------------|-------------------------|--------------------------------|----|----|----|----------|--|
|   |                     |               |                       |                         | 10                             | 30 | 50 | 95 |          |  |
| Zinc chloride                                   | 1.028               | 20            | ...                   | ...                     | Same as water                  |    |    |    | Odorless | Contained 2.67% ZnCl <sub>2</sub>            |
| Zinc sulphate                                   | 1.033               | 20            | ...                   | ...                     | Same as water                  |    |    |    | Odorless | " 5.9% ZnSO <sub>4</sub> 7H <sub>2</sub> O   |
| Zinc sulphate<br>(by-product)                   | 1.040               | 20            | ...                   | ...                     | Same as water                  |    |    |    | Odorless | " 6.8% ZnSO <sub>4</sub> 7H <sub>2</sub> O   |
| Sapwood antiseptic                              | 1.027               | 20            | ...                   | ...                     | Same as water                  |    |    |    | Odorless | " 2.92 % NaCl                                |
|   |                     |               |                       |                         |                                |    |    |    |          | " .246% CaSO <sub>4</sub>                    |
|   |                     |               |                       |                         |                                |    |    |    |          | " .246% ZnSO <sub>4</sub> 7 H <sub>2</sub> O |
|   |                     |               |                       |                         |                                |    |    |    |          | " .182% CuSO <sub>4</sub> 5 H <sub>2</sub> O |
|   |                     |               |                       |                         |                                |    |    |    |          | " .06 % FeSO <sub>4</sub> 4 H <sub>2</sub> O |
|   |                     |               |                       |                         |                                |    |    |    |          | " 0.93% Al. sulphate                         |
| B. M. Preservative                              | 1.025               | 20            | ...                   | ...                     | Same as water                  |    |    |    | Odorless | " 1.8% ZnCl <sub>2</sub>                     |
| Sodium silicate                                 | 1.074               | 20            | ...                   | ...                     | Same as water                  |    |    |    | Odorless | " 8.9% Sodium silicate                       |
| Sodium fluoride                                 | 1.009               | 20            | ...                   | ...                     | Same as water                  |    |    |    | Odorless | " 1.2% Sodium fluoride                       |
| Cresol calcium                                  | 1.075               | 20            | ...                   | ...                     | Same as water                  |    |    |    | Odorless | 2.43% Cresol calcium solution                |

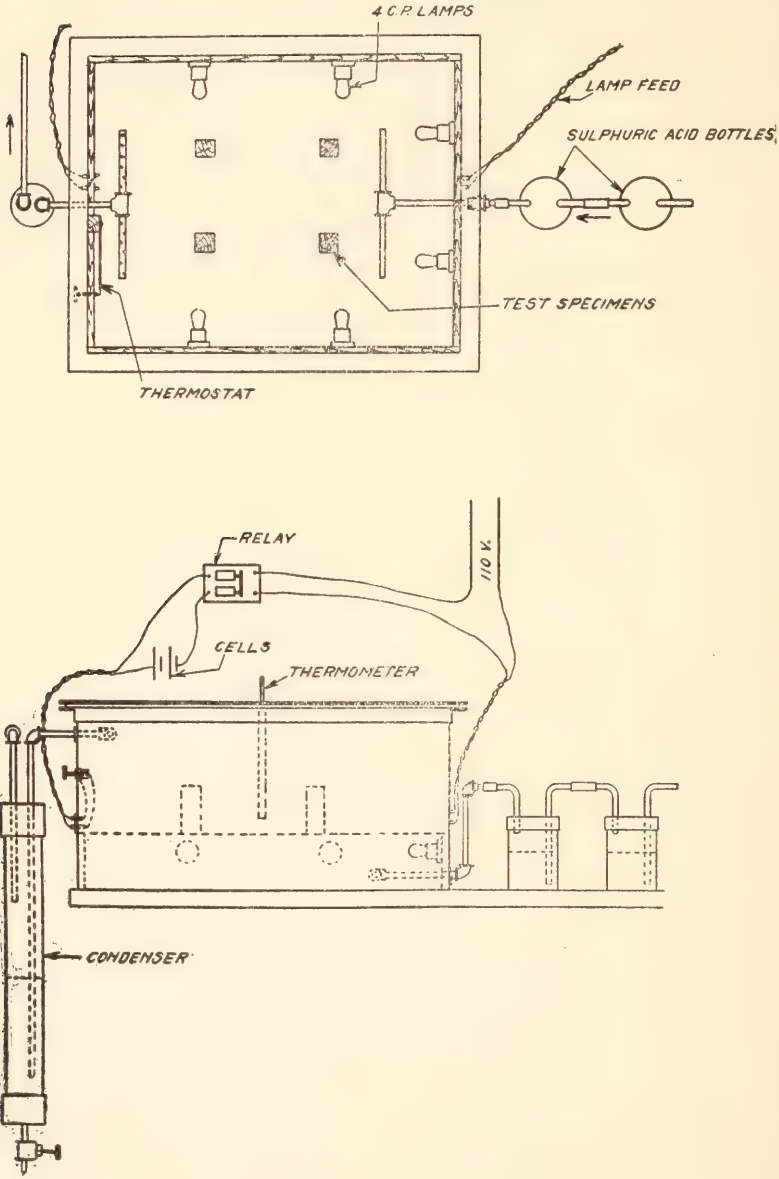


Figure 4. VOLATILITY APPARATUS

and its amount determined by an analysis of the acid solution. The deposited metal thus obtained was added to the loss of iron and this total represented the total corrosion.

### *Paint Tests*

The treated wood was first air-seasoned for about one month and then coated with white paint (30 pounds of lead oxide to one gallon of linseed oil), noting the color change which subsequently took place.

### RESULTS

In the following brief summary of results already secured the author wishes to strongly emphasize that they are tentative only and may be changed in view of subsequent tests, as the field covered is new and errors in manipulation, not at present apparent, might exist. Every feasible precaution, however, was taken to avoid errors and when these were uncontrollable they are so mentioned.

#### *Effect of the Preservative on the Strength of Wood* (for details see Table 3)

As a greater accuracy than plus or minus ten per cent could not be obtained in these tests, largely because of variables inherent in wood, the following conclusions should be interpreted liberally:

1. All of the preserving oils, *viz.*, coal-tar creosote, hardwood tar, wood creosote, 1.07 oil, and copperized oil, produced, *per se*, no appreciable weakening in the strength of the wood impregnated with them. The increases in strength noted in some cases were probably due to a lower moisture content in the treated specimens at the time of test. The amount of moisture which they contained could not be definitely determined, although it is believed to be below six per cent.

2. In general, the water-soluble preservatives caused a slight weakening of the seasoned wood. This was most pronounced in the case of sodium silicate and by-product zinc sulphate. The values given for the effect of these preservatives are accentuated, due to the higher moisture content of the treated pieces. The application of a moisture correction factor would probably show that with the exception of sodium silicate and by-product zinc

sulphate the weakening caused by these water-soluble preservatives is of no practical significance.

*Penetrance of the Preservative into Wood* (for details see Table 3)

TABLE 3.—PENETRANCE OF THE PRESERVATIVES AND THEIR EFFECT ON THE STRENGTH OF WOOD

| Preservative designated by co-operator as | Penetration    |       |                   |      | Average absorption of preservative | Strength in per cent of modulus of rupture of untreated wood | Moisture at Test |         |
|---|----------------|-------|-------------------|------|------------------------------------|--|------------------|---------|
|   | Rad. and Tang. |       | Long <sup>1</sup> |      |                                    |  | Untreated        | Treated |
|   | Max.           | Min.  | Max.              | Min. |                                    |  |                  |         |
|   | In.            | In.   | In.               | In.  |                                    |  |                  |         |
| Coal-tar creosote                         | 0.28           | 0.23  | 6.0               | 5.3  | 8.76                               | 93   | 6.2              | ....    |
| S.P.F. Carbolineum                        | 0.37           | 0.23  | 6.0               | 5.7+ | 8.83                               | ....   | ....             | ....    |
| Avenarius Ca bolineum                     | 0.17           | 0.12  | 6.0               | 5.3+ | 8.08                               | 109  | 6.81             | ....    |
| Hardwood tar                              | 0.03           | 0.03  | 0.92              | 0.50 | 6.50                               | 98   | 6.11             | ....    |
| Creosote (Douglas fir)                    | 0.08           | 0.08  | 3.58              | 2.33 | 2.82                               | 107  | 5.8              | ....    |
| 1.07 oil                                  | 0.10           | 0.10  | 6.0               | 3.33 | 9.58                               | 108  | 4.52             | ....    |
| Timberasphalt                             | 0.02           | 0.02  | 0.33              | 0.33 | 5.68                               | 106  | 6.68             | ....    |
| Copperized oil                            | 0.22           | 0.22  | 6.0               | 4.08 | 8.58                               | 101  | 5.49             | ....    |
| Zinc chloride                             | 0.10           | 0.083 | 6.0               | 5.3  | 0.43a                              | 88   | 7.13             | 9.35    |
| Zinc sulphate (by-product)                | 0.25           | 0.17  | 6.0               | 4.66 | 1.11b                              | 82   | 3.88             | 5.77    |
| Zinc sulphate                             | 0.10           | 0.08  | 6.0               | 4.66 | 0.96b                              | 89   | 5.14             | 9.6     |
| Cresol calcium                            | 0.10           | 0.10  | 6.0               | 3.30 | 0.46                               | 103  | 5.72             | 6.58    |
| B. M. preservative                        | 0.13           | 0.10  | 6.0               | 4.6  | 0.50b                              | 85   | 5.16             | 9.48    |
| Sodium silicate                           | 0.05           | 0.03  | 0.46              | 0.30 | 0.99                               | 82   | 6.42             | 7.38    |
| Sodium fluoride                           | 0.10           | 0.10  | 6.0               | 5.00 | 0.20                               | 85   | 5.82             | 8.7     |

<sup>1</sup> A penetration of 6 inches was the maximum that could be secured. The absorptions here given have no reference to the data on penetrance.

(a) Dry salt. (b) For composition, see Table 2.

3. The following preservatives, so far as penetrance is concerned, can be considered satisfactory: Coal-tar creosote, S.P.F. and Avenarius carbolineums, 1.07 oil, copperized oil, zinc chloride, zinc sulphate, cresol calcium, B. M. preservative, and sodium fluoride.

4. The "creosote" from Douglas fir was very difficult to force through hemlock, being about twice as resistant as coal-tar creosote.

5. Satisfactory penetrations with hardwood tar, Timberasphalt, and sodium silicate were not secured. The results indicated that



they are from six to eighteen times as resistant to impregnation as the preservatives mentioned in conclusion (3).

*Permanence of the Preservative after Injection into Wood* (for details see Table 4)

TABLE 4.—PERMANENCE OF THE PRESERVATIVE AFTER INJECTION INTO WOOD

| Preservative designated by co-operator as | Leaching   |         |         |         |         | Volatility                               |         |         |         |         |         |
|---|--|---------|---------|---------|---------|--|---------|---------|---------|---------|---------|
|   | Per cent dry salt leached after Immersion in Water for |         |         |         |         | Per cent volatilized after seasoning for |         |         |         |         |         |
|   | 5 days   | 10 days | 15 days | 20 days | 30 days | 10 days                                  | 20 days | 30 days | 50 days | 70 days | 90 days |
| Coal-tar <sup>1</sup> creosote            | ..   | ..      | ..      | ..      | ..      | 13                                       | 20      | 24      | 28      | 30      | 32      |
| Coal-tar creosote Frac. 1 <sup>1</sup>    | ..   | ..      | ..      | ..      | ..      | 13                                       | 21      | 26      | 32      | 36      | ..      |
| Coal-tar creosote Frac. 2 <sup>1</sup>    | ..   | ..      | ..      | ..      | ..      | 8  | 12      | 16      | 20      | 22      | ..      |
| Coal-tar creosote Frac. 3 <sup>1</sup>    | ..   | ..      | ..      | ..      | ..      | 7  | 10      | 12      | 15      | 17      | ..      |
| Coal-tar creosote Frac. 4 <sup>1</sup>    | ..   | ..      | ..      | ..      | ..      | 3  | 4       | 4.5     | 5.0     | ..      | ..      |
| Coal-tar creosote Frac. 5 <sup>1</sup>    | ..   | ..      | ..      | ..      | ..      | 1.8                                      | 2.5     | 3.0     | 4.0     | ..      | ..      |
| Hardwood tar                              | ..   | ..      | ..      | ..      | ..      | 11                                       | 12      | 13      | 19      | 20      | 22      |
| Wood creosote (Douglas fir)               | ..   | ..      | ..      | ..      | ..      | 11                                       | 11      | 17      | 19      | 20      | 28      |
| 1.07 oil                                  | ..   | ..      | ..      | ..      | ..      | 11                                       | 8       | 11      | 12      | 14      | 18      |
| Copperized oil                            | ..   | ..      | ..      | ..      | ..      | 1  | 2       | 4       | 6       | 9       | 11      |
| Zinc chloride                             | 46   | 54      | 57      | 60      | 62      | ..                                       | ..      | ..      | ..      | ..      | ..      |
| Zinc sulphate                             | 42   | 50      | 53      | 56      | 59      | ..                                       | ..      | ..      | ..      | ..      | ..      |
| Zinc sulphate (by-product)                | 47   | 57      | 63      | 65      | 68      | ..                                       | ..      | ..      | ..      | ..      | ..      |
| Cresol calcium <sup>2</sup>               | 21   | 26      | 28      | 31      | 33      | ..                                       | ..      | ..      | ..      | ..      | ..      |
| B. M. preservative <sup>3</sup>           | 43   | 47      | 51      | 54      | 57      | ..                                       | ..      | ..      | ..      | ..      | ..      |

6. After three months' exposure about one-third of the coal-tar creosote injected into the test specimens had volatilized. This was about 4 per cent more than for creosote from Douglas fir, 10 per cent more than for hardwood tar, 14 per cent more than for 1.07 oil, and 21 per cent more than for copperized oil, tested under similar conditions.

<sup>1</sup> The volatility of these fractions are comparable only to each other. Their volatilization should not be compared with that of the other preservatives. For absorption of preservative, see Table 3.

<sup>2</sup> Percentage of calcium; cresols not determined.

<sup>3</sup> Percentage of zinc chloride only.

8. The volatility of coal-tar creosote fractions was proportional to their distillation. Fractions with low ranges, *ceteris paribus*, are less stable than those with high. At the end of one month the lowest had lost about eight times as much as the highest.

*Effect of the Preservative on the Combustibility of Wood* (for details see Table 5)

TABLE 5.—INFLAMMABILITY OF TREATED WOOD

| Preservative designated by co-operator as | Temperature of Ignition C. |                  | Loss in weight due to burning calculated in % of weight before ignition |    | Character of Combustion                            |
|---|----------------------------|------------------|---|----|--|
|   | Days after Impregnation    |                  | Days seasoned   |    |  |
|   | 2                          | 90               | 2   | 90 |  |
| Untreated wood                            | 320                        | ....             | 29  | .. | Burned freely                                      |
| Coal-tar creosote                         | 173                        | 216              | 40  | 27 | Burned freely, black smoke, easily extinguished    |
| S.P.F. carbolineum                        | 243                        | ....             | 26  | .. | Burned like coal-tar creosote but not so freely    |
| Avenarius carbo-lineum                    | 213                        | ....             | 32  | .. | Burned like coal-tar creosote but not so freely    |
| Hardwood tar                              | 190                        | 241              | 29  | 30 | Burned freely, dense black smoke                   |
| Wood creosote (Douglas fir)               | 167                        | 217              | 36  | 26 | Burned like coal-tar creosote                      |
| 1.07 oil                                  | 231                        | 243              | 40  | 31 | Burned like avenarius carbolineum                  |
| Timberasphalt                             | 296                        | ....             | 28  | .. | Did not burn freely                                |
| Copperized oil                            | 200                        | 228              | 43  | 33 | Burned like coal-tar creosote                      |
| Zinc chloride                             | ...                        | 287 <sup>1</sup> | ..  | 19 | Hard to ignite, burned poorly, easily extinguished |
| Zinc sulphate                             | ...                        | 304 <sup>8</sup> | ..  | 18 | Hard to ignite, burned poorly, easily extinguished |
| Zinc sulphate (by-product)                | ...                        | 298 <sup>1</sup> | ..  | 15 | Hard to ignite, burned poorly, easily extinguished |
| Cresol calcium                            | ...                        | 288 <sup>1</sup> | ..  | 29 | Burned freely, white smoke hard to extinguish      |
| B. M. preservative                        | ...                        | 305 <sup>1</sup> | ..  | 18 | More difficult to burn than zinc chloride          |
| Sodium silicate                           | ...                        | 309 <sup>1</sup> | ..  | 10 | More difficult to burn than B. M. preservative     |
| Sodium fluoride                           | ...                        | 303 <sup>1</sup> | ..  | 25 | Burned like zinc chloride                          |

<sup>1</sup> Woods treated with salts were ignited as soon as their moisture content was reduced by air seasoning to 6%, usually about two weeks after impregnation. For absorption of preservative, see Table 3.

NOTE.—All salts burned for less than three minutes. All oils burned for three minutes and were then extinguished.

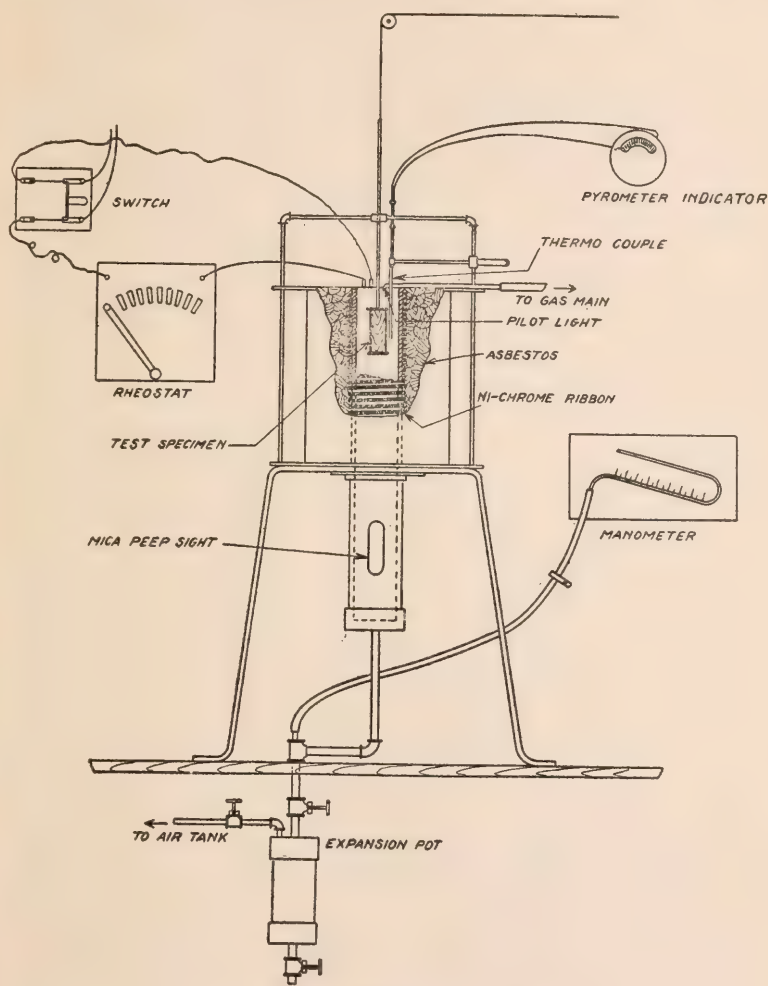


Figure 5. INFLAMMABILITY APPARATUS

7. After one month's leaching, nearly two-thirds of the zinc chloride injected into the wood had leached. This loss was 38 per cent greater than the amount of coal-tar creosote which volatilized during the same period. It should be noted, however, that the test for leaching was much more severe than the test for volatilization.

9. Wood treated with the oils in every case ignited at lower temperatures than untreated wood. When permitted to air-season for three months the temperature of ignition was considerably raised, due probably to the evaporation of the more volatile constituents. The loss in weight from burning treated wood seasoned for three months was also less than in the specimens burned shortly after impregnation (exception — hardwood tar).

TABLE 6.—TOXICITY OF PRESERVATIVES

(As determined by the Petri-dish method against *Fomes Annosus*, Fr.)

0=no growth. 1=slight growth. 2=retarded growth. 3=strong growth

| PER CENT OF PRESERVATIVE | PRESERVATIVES DESIGNATED BY CO-OPERATOR AS |                              |                              |                              |                              |                              |                    |                       |              |                             |          |               |                |          |               |                    |
|--------------------------|--|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|--------------------|-----------------------|--------------|-----------------------------|----------|---------------|----------------|----------|---------------|--------------------|
|                          | Coal-tar Creosote                          | Coal-tar Creosote Fraction 1 | Coal-tar Creosote Fraction 2 | Coal-tar Creosote Fraction 3 | Coal-tar Creosote Fraction 4 | Coal-tar Creosote Fraction 5 | S.P.F. Carbolineum | Avenarius Carbolineum | Hardwood Tar | Wood Creosote (Douglas fir) | 1.07 Oil | Timberasphalt | Copperized Oil | Fuel Oil | Zinc Chloride | Sapwood Antiseptic |
| .2                       | 1  | 2 <sup>1</sup>               | 0                            | 1                            | 1                            | 2                            | 2                  | 2                     | 3            | 2                           | 3        | 3             | 3              | 3        | 1             | 3                  |
| .4                       | 0  | 0                            | 0                            | 0                            | 0                            | 2                            | 1                  | 1                     | 2            | ...                         | 3        | 3             | 3              | 3        | 0             | 3                  |
| .6                       | ...  | ...                          | ...                          | ...                          | ...                          | 2                            | 0                  | 0                     | ...          | ...                         | 3        | 3             | 3              | 3        | ...           | 3                  |
| .8                       | ...  | ...                          | ...                          | ...                          | ...                          | 2                            | ...                | ...                   | ...          | ...                         | 3        | 3             | 3              | 3        | ...           | 3                  |
| 1.0                      | ...  | ...                          | ...                          | ...                          | ...                          | 2                            | ...                | ...                   | ...          | ...                         | 3        | 3             | 3              | 3        | ...           | 3                  |
| 2.0                      | ...  | ...                          | ...                          | ...                          | ...                          | 2                            | ...                | ...                   | ...          | ...                         | 3        | ...           | 3              | ...      | ...           | 3                  |
| 3.0                      | ...  | ...                          | ...                          | ...                          | ...                          | 2                            | ...                | ...                   | ...          | ...                         | 3        | ...           | 3              | ...      | ...           | 3                  |
| 4.0                      | ...  | ...                          | ...                          | ...                          | ...                          | ...                          | ...                | ...                   | ...          | ...                         | ...      | ...           | ...            | ...      | ...           | 3                  |
| 5.0                      | ...  | ...                          | ...                          | ...                          | ...                          | ...                          | ...                | ...                   | ...          | ...                         | ...      | ...           | ...            | ...      | ...           | 3 <sup>2</sup>     |

10. In general, wood treated with the water-soluble preservatives ignited at higher temperatures than wood treated with oils, although the temperature of ignition was lower than the untreated wood.<sup>3</sup> Furthermore, wood treated with the water-soluble salts showed in general a less loss in weight after combustion than those treated with the oils. It should be noted, however, that the

<sup>1</sup>Creosote Fraction 1 is so volatile that concordant results are difficult to obtain. At the close of the experiment it is probable that much of the preservative had evaporated from the medium—which may account for the low toxicity indicated.

<sup>2</sup>Slight growth at 75 per cent.

<sup>3</sup>Wood dipped in a 50 per cent sodium silicate solution ignited at a temperature of 448° C. and its weight was reduced 17 per cent, although it immediately extinguished when dropped in the lower chamber of the inflammability apparatus.

amount of wood actually burned may have been greater than in the case of oils.

11. Untreated wood and wood treated with oils (exception — Timberasphalt) burned freely and in general had to be extinguished after a 3-minute period, while wood treated with water-soluble salts (exception — cresol calcium) burned slowly and became extinguished in less than three minutes.

*Toxic Efficiency of the Preservative in Inhibiting Fungous Growth*  
(for details see Table 6)

The following tentative conclusions on the toxicity of the various preservatives may be drawn, although the author wishes to emphasize that they should not as yet be considered final, due to errors peculiar to the Petri-dish method.

12. Zinc chloride and coal-tar creosote offered about the same resistance to the growth of a wood-destroying fungus.

13. The toxicities of the coal-tar creosote fractions distilling below 320° C. were quite similar to each other and to coal-tar creosote.

14. Those portions of coal-tar creosote distilling above 320° C. were but slightly toxic, being at least fifteen times less resistant than the creosote itself.

15. The toxicity of preservatives designated as S.P.F. and Avenarius carbolineums was quite similar, being somewhat less than that for the coal-tar creosote tested.

16. Preservatives designated as 1.07 oil, Timberasphalt, copperized oil, fuel oil, and Sapwood Antiseptic all had no effect in inhibiting fungous growth up to concentrations of at least one per cent.

The methods of determining toxicity by pure-culture-jar and fungus-pit tests have, up to this writing, not progressed sufficiently far to yield definite results.

Although too few determinations have been made to date to draw final conclusions, nevertheless those which have been made indicate that the ball test should prove highly valuable in determining mechanically the extent of decay in wood.



*Corrosive Action of the Preservative on Flange Steel* (for details see Table 7)

17. Of the various preservatives tested, coal-tar creosote and copperized oil had the least deleterious effect on steel and their action in practical operations can very probably be neglected.

TABLE 7.—CORROSIVE ACTION OF THE PRESERVATIVE

| PRESERVATIVE DESIGNATED BY<br>CO-OPERATOR AS | LOSS IN WEIGHT (GRAMS) OF FLANGE STEEL<br>AFTER IMMERSION IN PRESERVATIVE AT 98°C. FOR |         |
|--|--|---------|
|  | 3 Weeks  | 4 Weeks |
| Coal-tar creosote                            | .0064  | .....   |
| Coal-tar creosote Frac. 1                    | .0000  | .0008   |
| Coal-tar creosote Frac. 2                    | .0389  | .0401   |
| Coal-tar creosote Frac. 3                    | .0063  | .0467   |
| Coal-tar creosote Frac. 4                    | .0313  | .0296   |
| Coal-tar creosote Frac. 5                    | .0005  | .0015   |
| Avenarius carbolineum                        | .0807  | .0951   |
| Hardwood tar                                 | 8.2629   | 11.2350 |
| Wood creosote (Douglas fir)                  | 5.0989   | .....   |
| Spiritine                                    | 1.2938   | 1.5029  |
| 1.07 oil                                     | .0243  | .....   |
| Timberasphalt                                | .2222  | .....   |
| Copperized oil                               | .0096  | .....   |
| Fuel oil                                     | .0012  | .0062   |
| Zinc chloride                                | 1.4636   | .....   |
| Zinc sulphate (a)                            | .6050  | .....   |
| Zinc sulphate (b) by-product                 | 1.3809   | .....   |
| B. M. preservative                           | 3.1660   | 4.1746  |
| Sodium fluoride                              | .1256  | .1588   |
| Cresol calcium                               | .0139  | .0181   |

(a) Equivalent to 2.1% zinc chloride solution.

(b) Equivalent to 6.2% zinc chloride solution.

For concentration of salt solutions used, see Table 2.

18. All the metallic salts were much more pronounced in their action than coal-tar creosote, so that the depreciation in plants using them would, unless precautionary measures were taken, be greater.

19. The very marked corrosion of hardwood tar and creosote from Douglas fir is probably due to the comparatively large amount of acetic acid which they contain.

*Discoloration of Painted Wood* (for details see Table 8)

20. All of the oils tested rendered the wood unfit for subsequent painting. Copperized oil was least objectionable in this respect.

If thoroughly dried after treatment so that excess oil would not appear on the surface, it is possible that wood treated with some of these preservatives could be satisfactorily painted with dark pigments.

TABLE 8.—DISCOLORATION OF PAINTED WOOD

| PRESERVATIVE DESIGNATED<br>BY CO-OPERATOR AS | CONDITION OF PAINTED SURFACE<br>AFTER EXPOSURE FOR ONE MONTH |
|--|--|
| Coal-tar creosote                            | Very badly discolored and paint not dry                      |
| Hardwood tar                                 | Very badly discolored and paint not dry                      |
| Wood creosote (Douglas fir)                  | Very badly discolored and paint not dry                      |
| 1.07 oil                                     | Very badly discolored and paint not dry                      |
| Copperized oil                               | Discolored, paint somewhat sticky                            |
| Zinc chloride                                | Appearance similar to the untreated specimen                 |
| Zinc sulphate (by-product)                   | Appearance similar to the untreated specimen                 |
| Zinc sulphate                                | Appearance similar to the untreated specimen                 |
| B. M. Preservative                           | Appearance similar to the untreated specimen                 |
| Sodium fluoride                              | Appearance similar to the untreated specimen                 |

21. The water-soluble salts were all satisfactory in that they caused no discoloration of the painted surface. If used under conditions where the wood is subjected to moist air, none of these preservatives might prove commercially satisfactory.

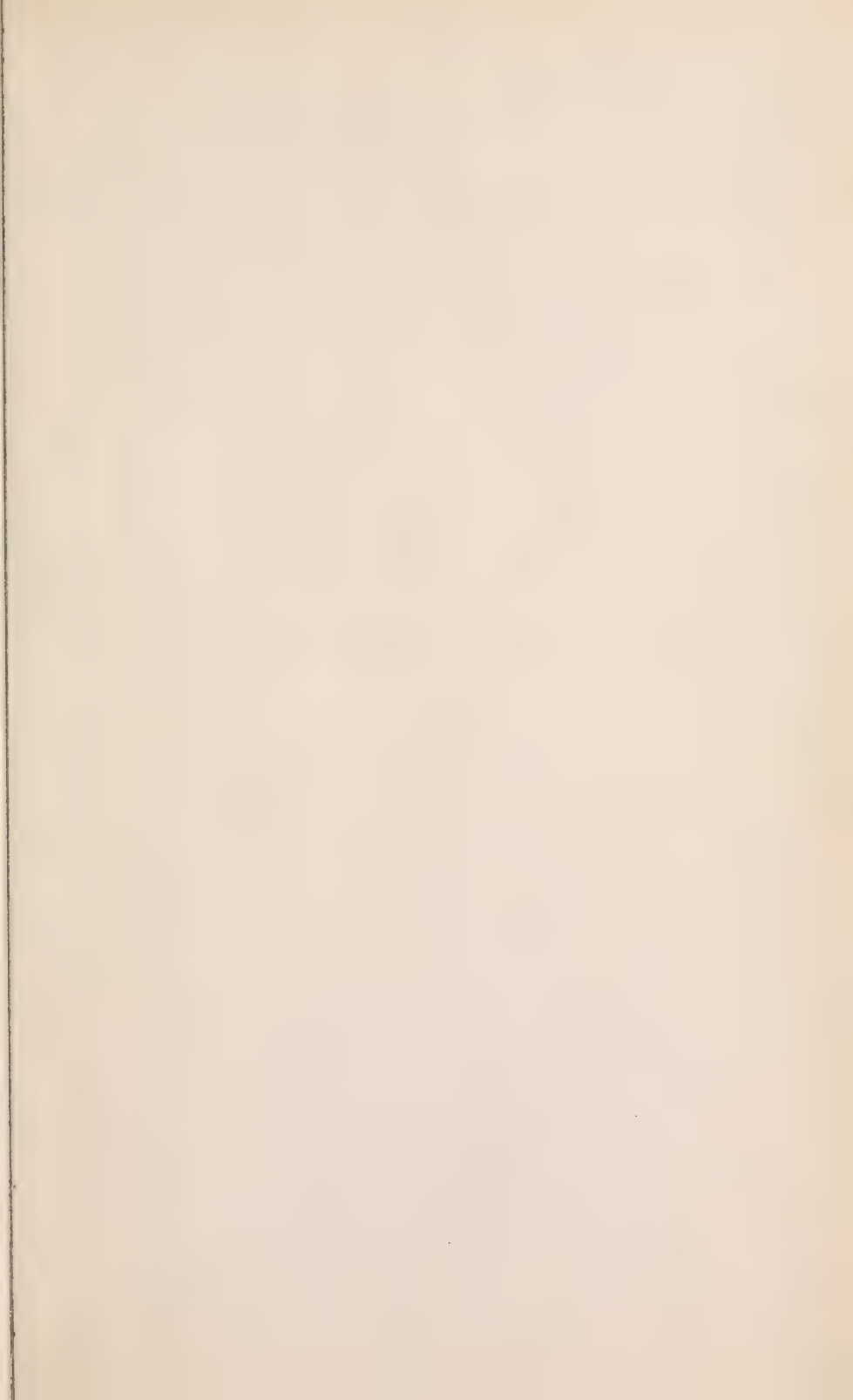
#### CONCLUSIONS

The depth to which oils can be impregnated varies as some inverse function of the viscosity. As temperature strongly influences the viscosity of oils, and as the diffusion of the preservative through the wood is one of the most important factors in proper treatment, it is concluded that to secure best results both the wood and the preservative should be heated to the proper temperature during the pressure period. Because of the low thermal conductivity of wood, the treatments should not be made too rapidly. With water-soluble salts these precautions are not important.

With coal-tar creosote it appears that the fractions of greatest stability are the least toxic. Present practice rather favors the retention in treated wood of the more volatile fractions by an admixture of the more stable ones. If the toxic values here given are correct, there is in practice being forced into wood about two

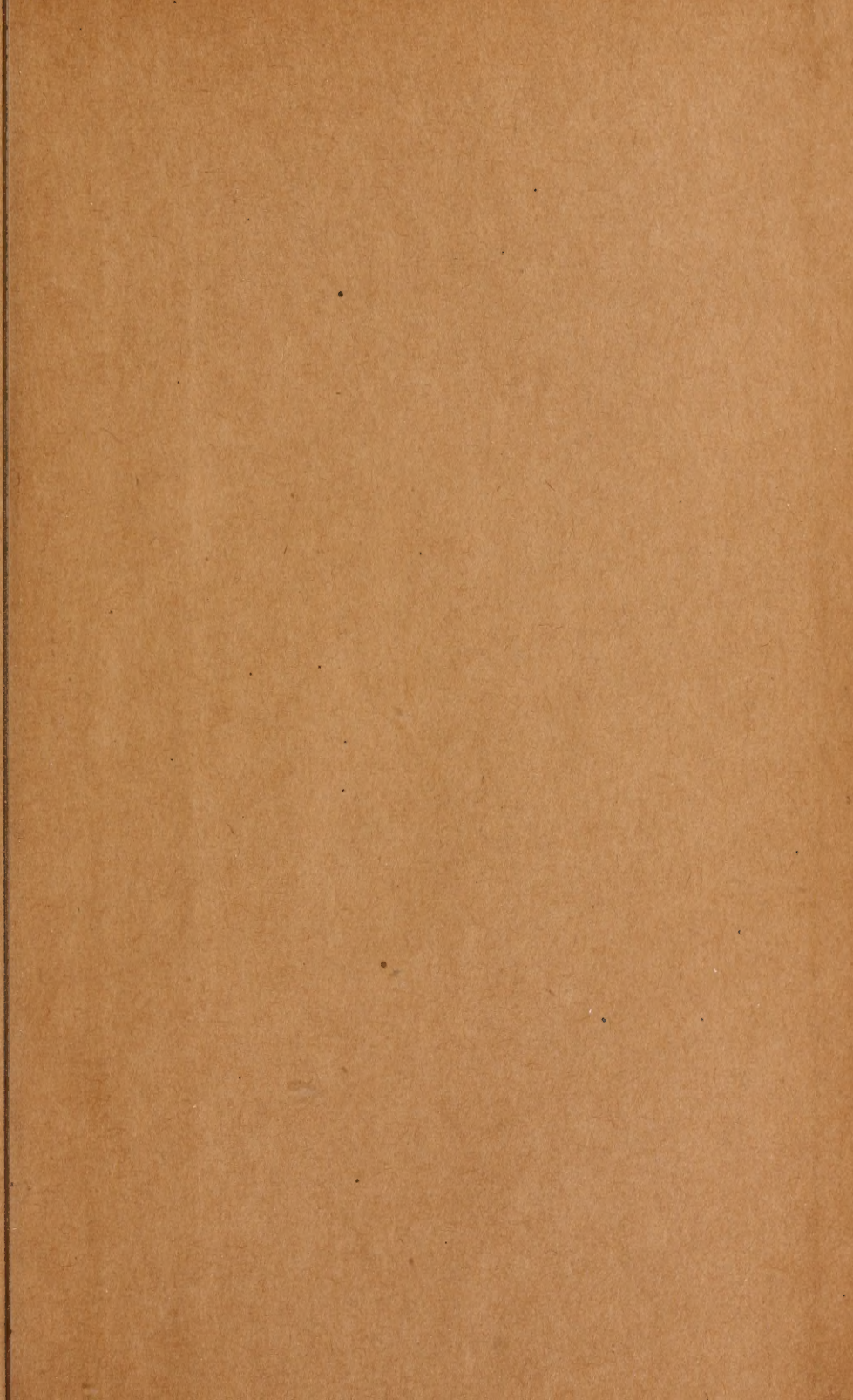
and one-half times as much zinc chloride and fifty times as much coal-tar creosote as is necessary to prevent decay. It is concluded therefore, that more economic results against decay, especially when it is accompanied by mechanical deterioration, can be secured by diffusing the preservative more thoroughly through the wood than by saturating the outer fibres and attempting to retain in the wood the volatile constituents through admixtures of nonvolatile constituents.

In general, the flash or burning point of an oil affects the inflammability of wood treated with it. Of greater importance, however, is the length of time the treated wood has seasoned, as a prolonged seasoning of such wood raises considerably its ignition temperature. It is concluded that it would be good practice to first season such treated timber before placing it in positions subject to fire. While wood treated with the water-soluble salts mentioned in these tests was in general less difficult to ignite than untreated wood, nevertheless the presence of such preservatives almost invariably renders the wood slow burning and easily extinguishable.













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